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IDENTIFICATION OF DECOMPOSITION PRODUCTS OF TROPYL

167

AZIDE AND INTERACTION OF TROPYLIUM ION

WITH NUCLEOPHILES

by

JAMES JOSEPH WARD, OCTOBER 10, 1943 -

A DISSERTATION

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI - ROLLA

In Partial Fulfillment of the Requirements for the Degree

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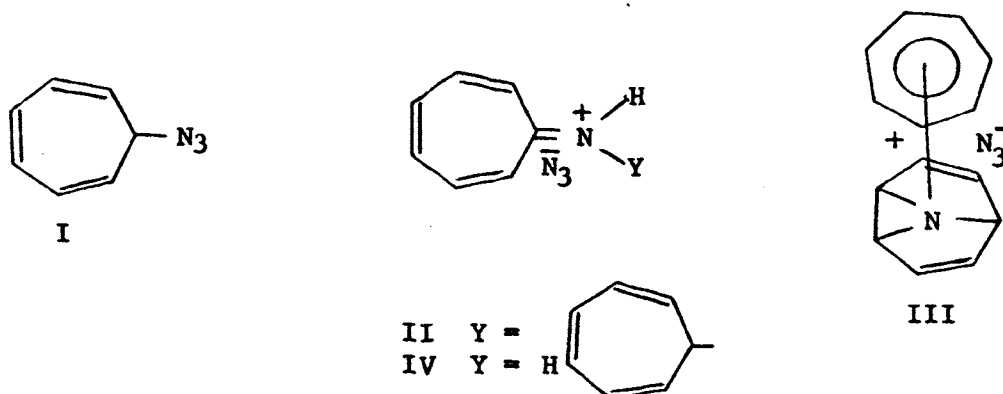
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"This thesis is dedicated to my wife, Karen, and my parents, Mr. & Mrs. J. M. Ward, whose encouragement and assistance made it possible."

ABSTRACT

An investigation of the structures of several of the products resulting from the decomposition of tropylium azide (I) and of the chemistry of related processes has been undertaken. Irradiation of samples of (I) in the vapor phase with low intensity UV G.E. Sun Lamps furnished a low melting white solid identified as tropylium troponimmonium azide (II). Earlier experiments of a similar nature reported to furnish (III) were not repeatable (Chem. Commun., 276 (1967)).



Upon standing, solutions of (I) slowly formed tropylium troponimmonium azide (IV) in the cold (J. Chem. Soc. (D), 220 (1970)). The structures (II) and (IV) were confirmed by conversion to the corresponding fluoborates and comparison with samples prepared by the methods of Bauld (J. Amer. Chem. Soc., 89, 6763 (1967)) and Dauben (ibid. 89, 6764 (1967)).

The nature of amine-tropylium ion interactions was investigated. The conclusions reported by P. B. Shevlin (Ph.D. Dissertation, Yale University, 1967) was at variance with those of D. S. Wulfman (Ph.D. Dissertation, Stanford University, 1962) and with those obtained in these laboratories as well as those reported by several other workers. We postulate, in contrast with Shevlin, that tropylium salts form at least 2 and possibly 4 different complexes with pyridine, none of which involves formation of a tightly held sigma complex in which an N-tropyl pyridinium species is present. Similar behavior was noted for 3,5 dimethyl pyridine. With 2 and 4 methylated pyridines, apparently C alkylation occurs. In these instances no evidence of reversible complex formation was observed.

Re-examination of dimethyl sulfoxide as a solvent for such studies reaffirmed the findings of Wulfman that sigma complex formation with solvent molecules occurred and precluded its use for equilibrium studies.

In hopes of gaining insight into the amine processes, the synthesis of a series of troyl acetates (acetate, chloracetate, dichloracetate) was undertaken. Only in the unsubstituted case was ester formed. In all cases tropone was obtained in fair yield. Only in one case was some tropilidene obtained. The mechanisms of these transformations are discussed.

ACKNOWLEDGMENTS

The author wishes to thank his advisor, Dr. D. S. Wulfman, Associate Professor of Chemistry, for his advice, assistance, and guidance during the course of this work.

For the financial assistance received from NDEA, NSF and the University of Missouri - Rolla, the author is deeply grateful.

The author wishes to acknowledge various personnel at Monsanto Company for the mass spectra run, and also Varian Associates for running various NMR spectra, and L. J. Durham, Stanford University, for NMR spectra run.

Thanks are extended to the many faculty members and graduate students of the Chemistry Department, University of Missouri - Rolla, for their suggestions and advice and the many discussions with them during the course of this work.

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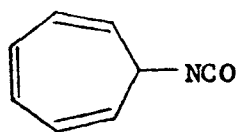
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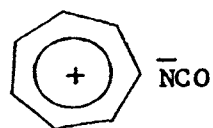
I. INTRODUCTION AND STATEMENT OF PROBLEM

The Wulfmans conducted a study of the two isomeric isocyanates reported by Dewar and Pettit¹ which had been assigned the structures (1) and (2). When it became apparent that (2) was in reality (3), an investigation of the isoelectronic azide was undertaken. The resulting material behaved as tropylium azide (4) in highly polar solvents (as evidenced by the ready availability of tropylium and azide ions) and as the covalent compound (5) in non-polar solvents as evidenced by the absence of ionic reactions.¹ An NMR study to determine whether the norcaradienyl species (6) might be present was undertaken with dielectric constant, ionic strength and temperature as variables.¹ The NMR studies indicated that troyl azide in polar media was forming the tropylium-azide ion pair and that the process most probably involved at least two azide ions per tropylium ion when exchange processes occurred.¹ In addition, a precipitate was observed when troyl azide solutions (or neat) were allowed to stand, even in sealed tubes under a nitrogen atmosphere. The NMR spectra of troyl azide, no matter how extensively purified, always showed at least trace amounts of an impurity which appeared at τ 5.20 (neat), and τ 4.40 in non polar solvents.

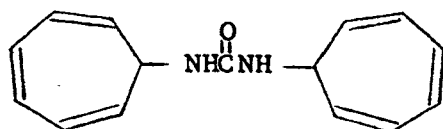
This impurity exhibited a single sharp resonance signal which was not noticeably altered by temperature variation over the range -80 to 80°. However no attempt was made at that time to determine if the signal observed might contain several types of protons with very similar chemical shifts. The field location of the NMR corresponded very nearly to the center of gravity of the troyl azide



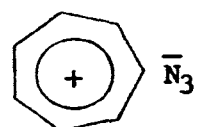
(1)



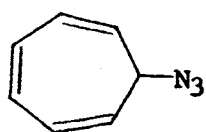
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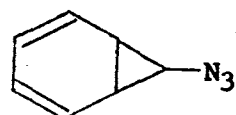
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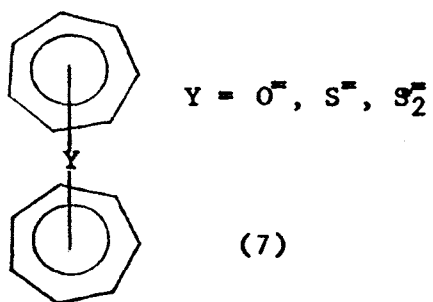
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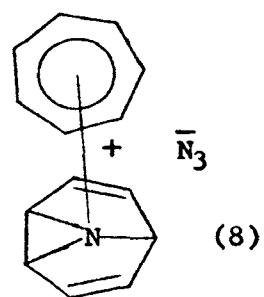
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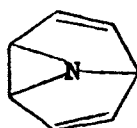
(6)



(7)



(8)



(9)

spectrum. This fact coupled with the single sharp resonance signal appeared consistent with a sandwich type compound (7) of which the only known examples exclusive of the metallocenes, were some cycloheptatrienyl systems reported by H. J. Dauben, Jr.²

D. S. Wulfman subsequently proposed this idea to Professor T. Brown (University of Illinois) who suggested that such materials as (7) might well be capable of existence. Wulfman subsequently prepared the ether, sulfide and disulfides which were examined by L. J. Durham and found to have typical tropyliene NMR spectra.

The present author undertook, as a senior research project, the synthesis of the corresponding selenium and tellurium compounds.³ The supposition was made that since tellurium and selenium had "available" f orbitals, the chances of forming sandwich compounds might be greater. The NMR spectra revealed normal tropyliene bonding (see Appendix 1).³

The present work developed as a continuation and expansion of the above work with the primary goal being the isolation and elucidation of structure and properties of the material responsible for the NMR signal at τ 4.40.

A comment by Professor E. C. Taylor (Princeton University) that infrared irradiation could readily bring about destruction of the azide chromophore in some azides lead us to suspect that a similar process might be occurring with troyl azide and that the extraneous peak was resulting from some form of azide - nitrene process. In an attempt to increase the amount of "impurity", troyl azide was irradiated in solution and in the vapor phase with infrared or ultraviolet.

The problem developed into attempts towards the isolation and characterization of the decomposition products from troyl azide and the examination of the interaction of troylium ion with various nucleophiles.

During the course of the work it became apparent that the interaction of nucleophiles and solvent molecules with troylium ion was little understood. Interactions of water, acetonitrile, and acetone, as solvents, with troylium ion made it impossible to observe the C^{13} -H coupling.⁵ The interaction of troylium perchlorate with triethylamine, pyridine, 2,6 dimethylpyridine, 2,4 dimethylpyridine, and 3,5 dimethylpyridine was investigated employing NMR spectroscopy.

The description and results of various unsuccessful attempts to isolate (9), appear as Appendix 3 to the thesis.

In order to further clarify the interactions of nucleophiles with troylium ion, syntheses of troyl acetate and the mono, di, and tri-chloroacetates were undertaken.

II. HISTORICAL

A. Properties and Reactions of Organic Azides

Organic azides were known before the turn of the century. In 1893 Michael reported that acetylenic esters react with alkyl azides to yield triazoles.⁶ Similar reactions were observed by Dimroth⁷ in 1910 and by Curtius and Klavehn in 1930.⁸ In 1912 and 1913 Wolff and Hercher reported that aryl azides react with olefins to yield 1,2,3 Δ^2 - triazolines.^{9,10} In 1916 Senior reported that triaryl-methyl azides rearrange thermally at 170° to 190° to benzophenone anils.¹¹ During the 1930's Alder and coworkers determined the reactivity of olefins toward aryl azides and found that unactivated olefins react slowly whereas strained bicyclic systems are particularly reactive.¹²⁻¹⁵

There was a resurgence of interest in organic azides in the early 1950's which has continued until the present time. This stemmed from the recognition that organic azides undergo several useful types of reactions and are rather important in the preparation of nitrogen-containing heterocycles. The decomposition of azides can lead to nitrenes and has been studied extensively.

A number of reviews and monographs have been published on or covering various aspects of azide chemistry.¹⁶⁻²²

The azide unit exhibits no visible spectrum and as a result organic azides are colorless unless other chromophores are present.²³ Dipole moment measurements indicate that the azide unit is more electronegative than carbon.^{24,25} The azide unit is linear, with the

organic residue at an angle of approximately 120° .²⁶ In azides the bond length between the two unsubstituted nitrogens (1.1\AA) is shorter than the other N-N bond (1.25\AA).²⁷

The infrared stretching frequency of covalent azides falls at 2140 cm^{-1} .²⁷ Ionic azides (NH_4N_3) show stretching frequency at about 2030 cm^{-1} .²⁸ Alkyl azides usually absorb weakly in the ultraviolet at approximately 287 nm and much more strongly at approximately 216 nm.²³ They are often explosive as well as toxic.

The reactions of organic azides may follow three basic routes. They may undergo 1,3 dipolar addition to an unsaturated system with or without subsequent loss of molecular nitrogen. They may rearrange with alkyl, aryl, or hydrogen migration and loss of molecular nitrogen. Lastly, they may lose molecular nitrogen to form nitrene intermediates which react further to yield the final product(s).

B. 1,3 Dipolar Additions

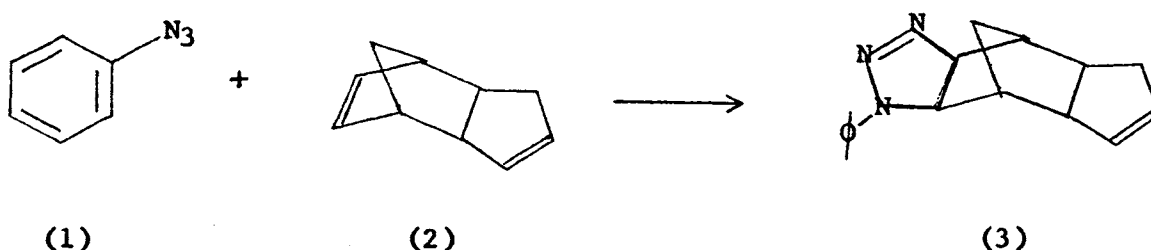
1. Triazoline Formation

The addition of an organic azide to an unsaturated system to form a 5-membered ring is one of the class of reactions known as 1,3 dipolar additions. This type of reaction has been described by Huisgen.^{16,29} Concerted cycloadditions of organic azides can be said to have the following properties: they have large negative entropies of activation, rather small enthalpies of activation, and the rates of reaction are almost independent of solvent polarity.^{30, 31,32,33}

In 1912 and 1913 Wolff and Hercher reported that aryl azides react with olefins to yield 1,2,3- Δ^2 -triazolines.^{9,10} The rates

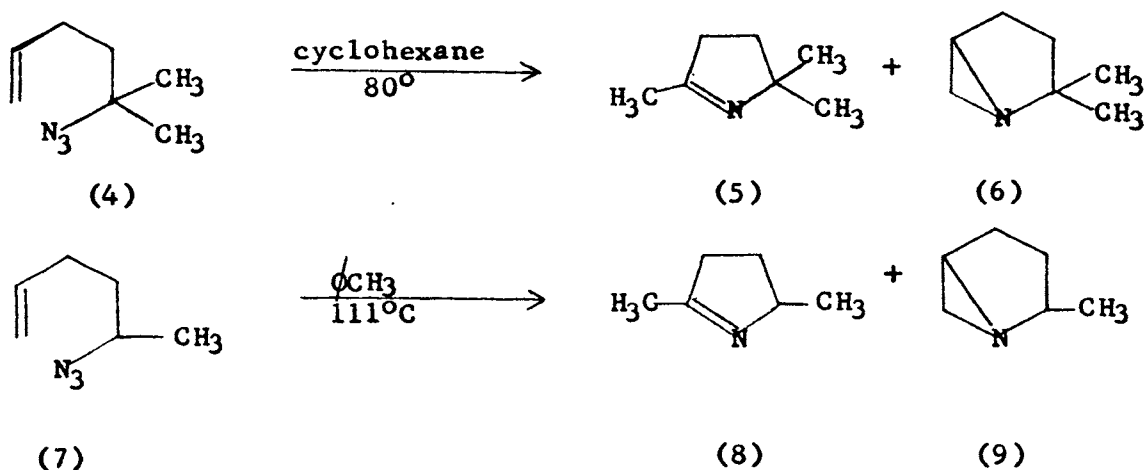
of these reactions are directly proportional to the strain of the double bond. Alder and coworkers determined that phenyl azide (1) reacts quantitatively with the strained double bond of dicyclopentadiene (2) (Chart 1).^{12,34}

Chart 1



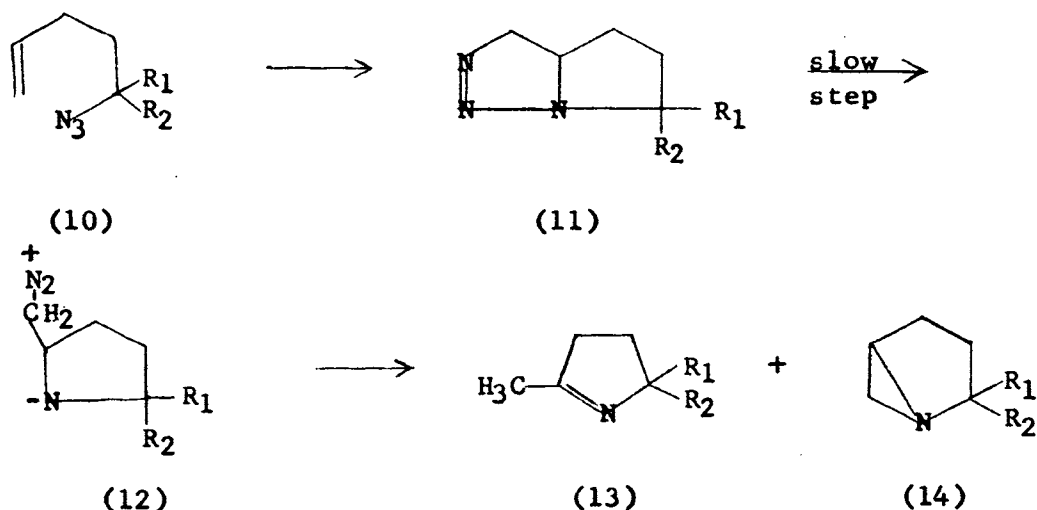
Most of the 1,2,3- Δ^2 -triazolines produced by 1,3 dipolar additions are thermally unstable, decomposing with loss of molecular nitrogen and subsequent rearrangement. Logothetis studied the decomposition of the olefinic azides (4) and (7)³⁵ (Chart 2).

Chart 2



The identity of the products was demonstrated by spectral analysis and independent synthesis. Logothetis suggested the mechanism in Chart 3 to account for the products.³⁵

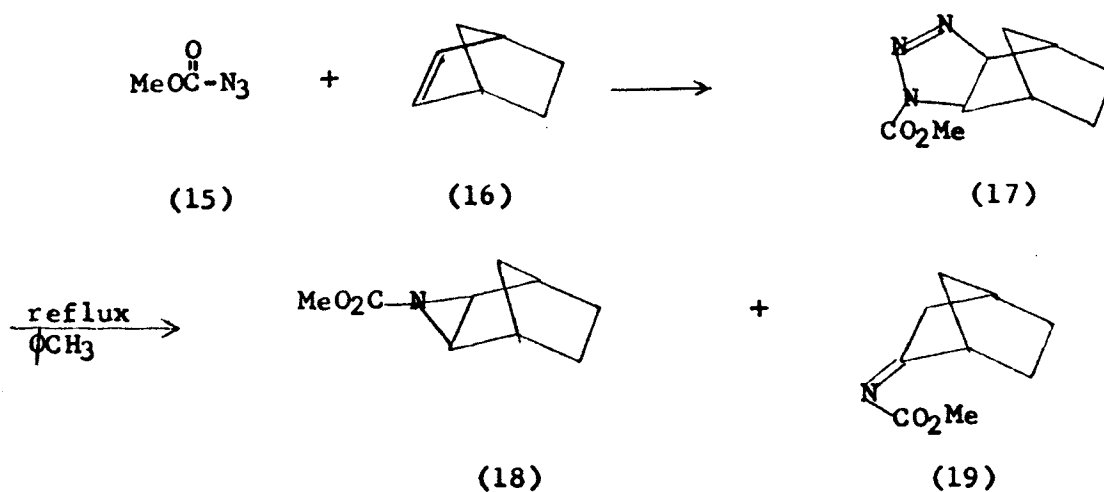
Chart 3



The parent azides when heated to 50°C. or allowed to stand at room temperature for two months gave quantitative yields of triazoline. These triazolines were then decomposed under identical conditions and furnished identical rate constants and products. There was no indication in this study of nitrenes as intermediates.

A similar mechanism has been proposed to account for the products obtained by Oehlschlager and coworkers (Chart 4) from methyl azidoformate and norbornene.³⁶

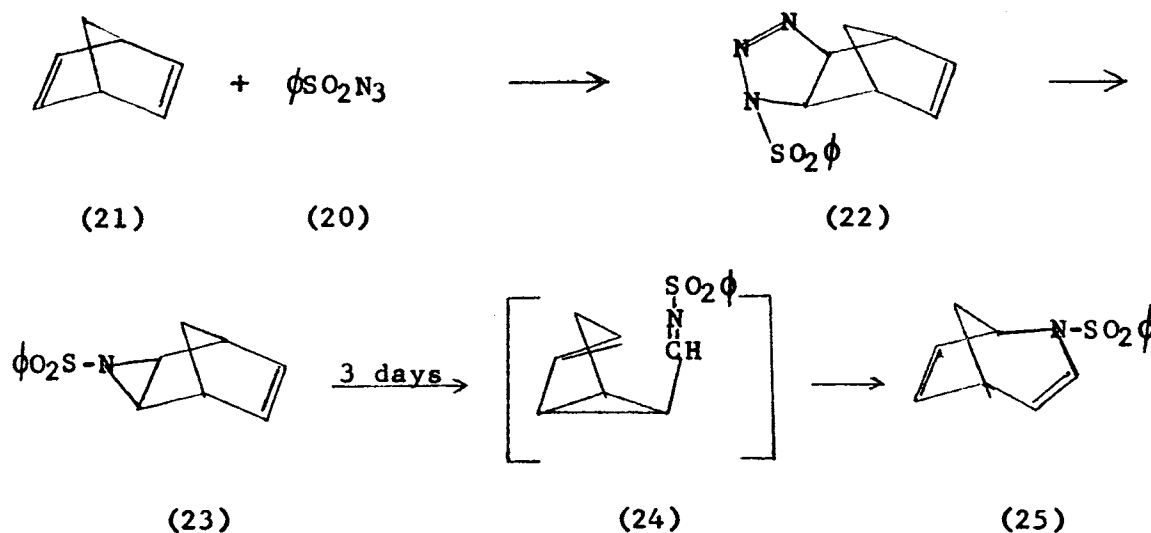
Chart 4



Consistent with a diazonium-betaine intermediate, the rate of nitrogen evolution is greatly increased by increasing solvent polarity.

Oehlschlager and Zalkow have studied the reaction of benzene-sulfonyl azide (20) with norbornadiene (21).³⁷ They showed that the reaction goes through the non-isolable triazoline (22) (Chart 5).

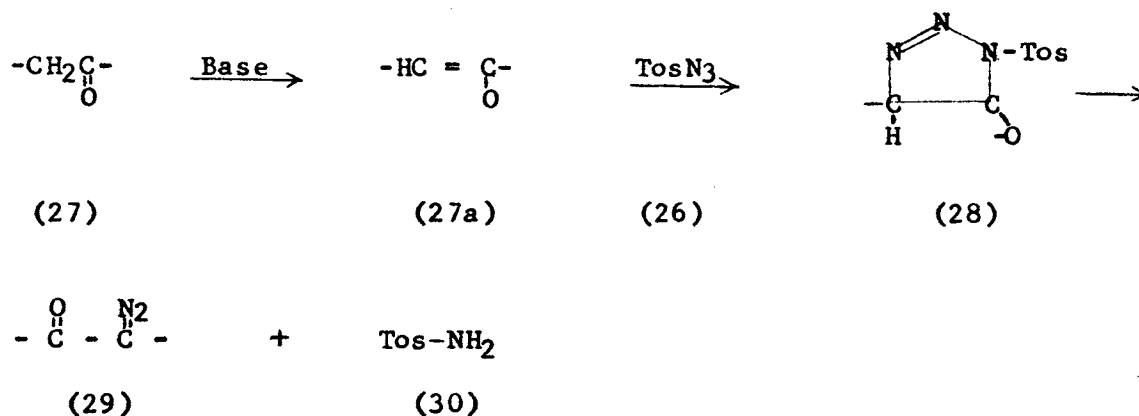
Chart 5



2. Diazo Transfer Reactions

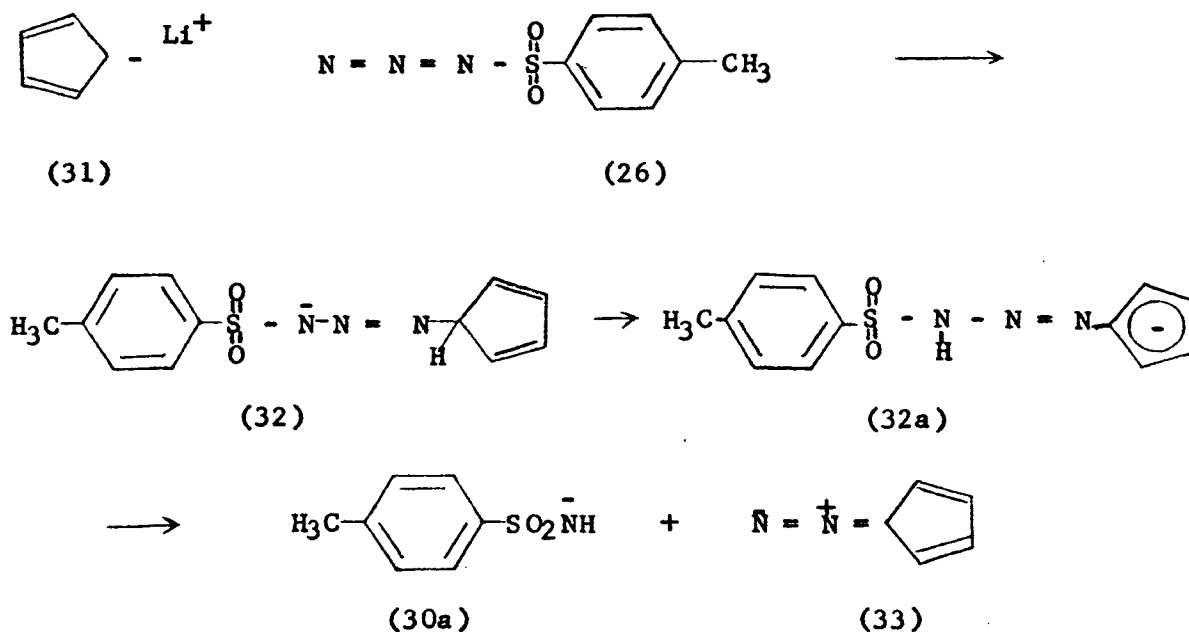
Most diazo transfer reactions (Chart 6) recently reported are a special case of 1,3 dipolar addition. In these reactions tosyl azide (26) reacts with an enolizable methylene compound (27) in the presence of a base to form an unstable triazoline (28) which decomposes to a diazo ketone (29) and tosyl amide (30). This reaction has been reviewed by Regitz.³⁸

Chart 6



There are certain cases of diazo transfer reactions which do not go through the triazoline intermediate. The work of Doering and De Puy³⁹ on the preparation of diazocyclopentadiene (34) is an example (Chart 7).

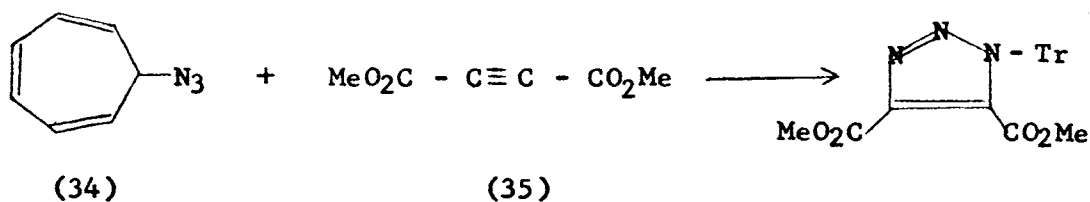
Chart 7



3. Triazole Formation

Organic azides can add to carbon-carbon triple bonds to form triazoles which are stable compounds. Looker⁴ studied the addition of tropyl azide (34) to various substituted acetylenes and found that tropyl azide (34) and dimethyl acetylene dicarboxylate (35) furnish the triazole (36) in 73% yield (Chart 8).

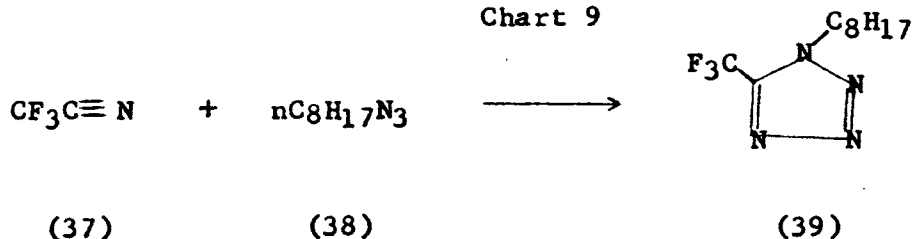
Chart 8



4. Tetrazole Formation

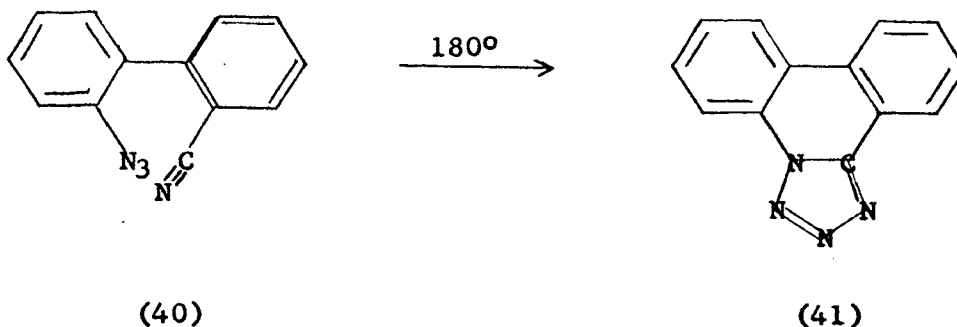
Organic azides can undergo dipolar additions with nitriles to yield tetrazoles (Chart 9), however the reaction is much slower than that with olefins. Intermolecular reactions occur only if the nitrile bears electron-withdrawing groups on the α carbon.⁴¹

Chart 9



Intramolecular reactions can occur with unactivated nitriles. Smith and coworkers⁴² studied the thermal cyclization of 2-azido-2'-cyanobiphenyl (40) to furnish the stable compound tetrazophenanthridine (41) which decomposes at 300° C. (Chart 10).

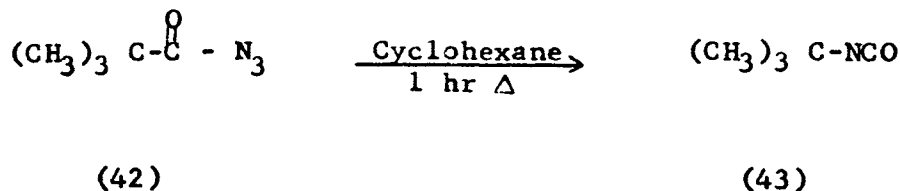
Chart 10



C. Concerted Loss of Nitrogen and Rearrangement

Some azide decompositions occur with loss of nitrogen under mild conditions and yield no nitrene-type products. The best explanation of these observations is that the loss of nitrogen and the reaction that occurs is a concerted process. There are no reports of any thermal Curtius rearrangements yielding nitrene type products. In the thermal Curtius rearrangement the 1,2 shift and loss of nitrogen seem to be concerted.⁴³ Lwowski and Tissue studied the thermal decomposition of pivaloyl azide (42) in cyclohexane.⁴⁴ They obtained an almost quantitative yield of t-butyl isocyanate (43) and could detect no nitrene type products in a system where 1% could have been detected.

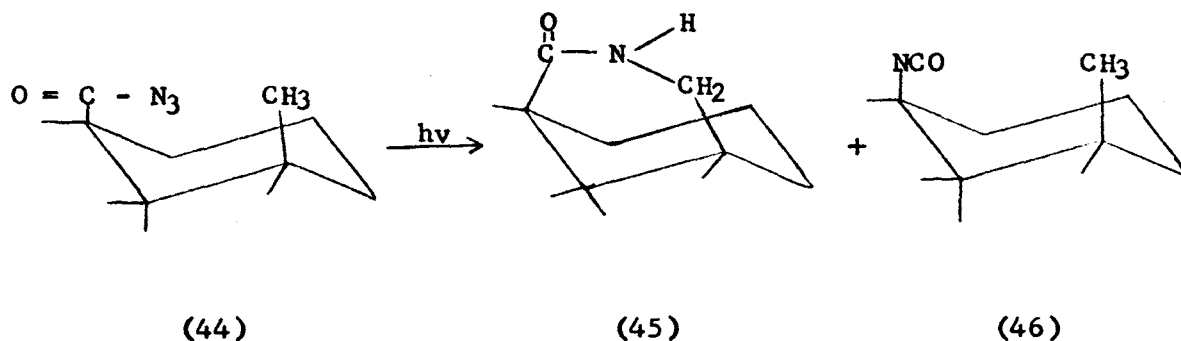
Chart 11



There are a few instances of nitrene-type products in photochemical

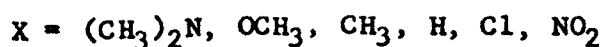
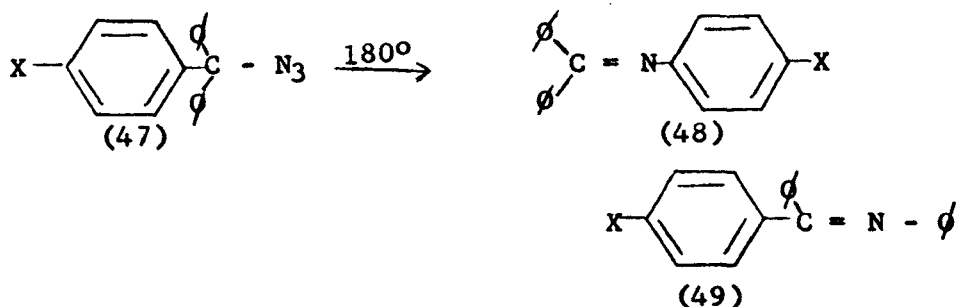
Curtius rearrangements; however, most of these are concerted. ApSimon and Edwards observed the reaction shown in Chart 12.⁴⁵

Chart 12



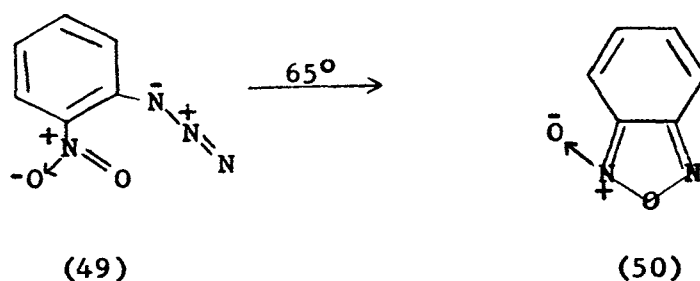
Saunders and Ware investigated the thermal conversion of para-substituted triarylmethyl azides (47) into benzophenone anils (48) (Chart 13).⁴⁶ They found that the reactions were always first order, that different *p*-substituted benzene rings had different migratory aptitudes, and that all substituted triarylmethyl azides react faster than the unsubstituted compound. These observations are best explained by a concerted mechanism.

Chart 13



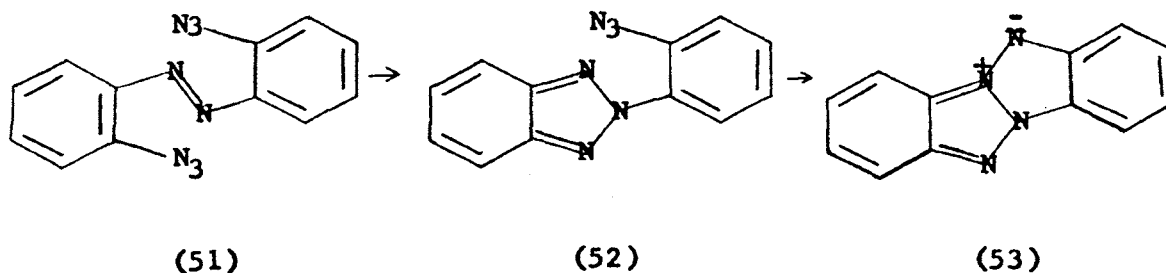
Some special cases are concerted reactions due to steric proximity of the azide moiety and the group with which it reacts. Fagley and coworkers studied the thermal decomposition of o-nitrophenyl azide (49) to benzofuroxan (50).⁴⁷ This reaction goes in nearly quantitative yield at 65° (Chart 14).

Chart 14



Carboni and coworkers⁴⁸ studied the thermal decomposition of 2,2'-diazidoazobenzene (51). This reaction is a two-step process (Chart 15). In the first step ring formation and nitrogen loss is a concerted process which occurs at 58° and yields 2(o-azidophenyl) 2-H-benzotriazole (52). The second step occurs only at much higher temperatures (170°) through a nitrene intermediate to yield dibenzo 1,3a,4,6a-tetraazapentalene (53).

Chart 15



D. Nitrene Reactions

Most photolyses of organic azides yield nitrenes, in both the vapor phase and in solution. Some, but not all, thermal decompositions of organic azides lead to nitrenes.

Considerable interest has been displayed in the nitrogen analog of carbenes. These electron-deficient neutral species will be called nitrenes in this thesis; however, the terms imidogens, imenes, imine radicals, azenes, azylenes and azacarbenes have appeared in the literature. There are three good reviews on nitrenes.¹⁷⁻¹⁹

These nitrenes once formed can stabilize themselves in several ways. They can isomerize to the imine, abstract hydrogen 1,5 and then cyclize to form pyrrolidines, dimerize to form an azo compound, insert into an aliphatic or aromatic carbon-hydrogen single bond, add across an olefinic or aromatic carbon-carbon double bond, add to various other unsaturated systems, and abstract hydrogen from the solvent.¹⁷⁻¹⁹

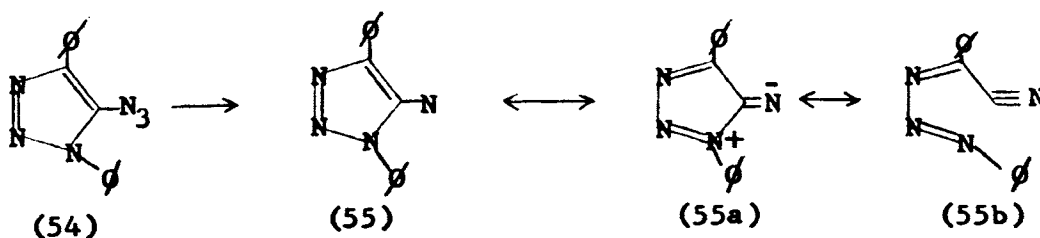
There has been some discussion of the electronic state of nitrenes generated by different processes. It is generally assumed that singlet nitrenes add to double bonds by a concerted mechanism, whereas triplet nitrenes first form an open chain triplet diradical followed by a spin inversion process prior to cyclization. Thus singlet nitrenes add in a stereospecific manner while triplet nitrenes add in a nonstereospecific manner.

Lwowski and McConaghy⁴⁹⁻⁵¹ have studied the addition of carbethoxynitrene to cis and trans 4-methyl-2-pentene. They found that

the reaction is stereospecific but that the degree of stereospecificity decreases with decreasing olefin concentration. They concluded that all the thermally-generated nitrenes were in the singlet state and two thirds of the photochemically-generated nitrenes were in the singlet state. They also concluded that addition of singlet nitrenes to the olefin competes with intersystem crossing to the triplet nitrene. Since intersystem crossing is favored by dilution this explains their results.

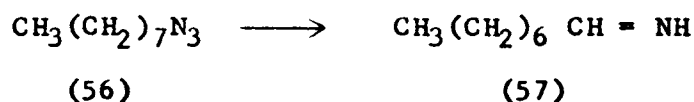
Smith and coworkers⁵² prepared what appears to be a stable nitrene. They found that 1,4 diphenyl-5-azidotriazole (54) loses one molecule of nitrogen at 50°. Labeling experiments using N¹⁵ showed that the nitrogen is lost from the azide unit. The solid does not follow any of the expected reaction routes of a nitrene. It has a three-peak NMR spectrum, shows only aromatic and carbon-nitrogen double bond and nitrogen-nitrogen double bond stretching in the IR spectrum, has a molecular weight close to that expected for this nitrene, and an electron paramagnetic resonance spectrum shows no unpaired electrons. It is soluble in petroleum ether, benzene, isopropyl alcohol, and acetone. The reaction yielding this compound and the proposed structure is shown in Chart 16. The structure was identified by a combination of chemical and spectral analysis.

Chart 16



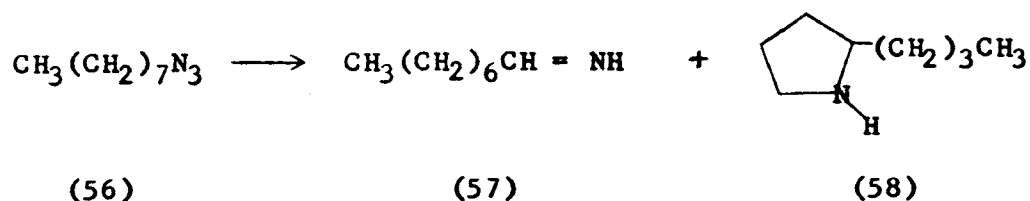
Barton and Morgan⁵³ decomposed thermally n-octyl azide (56) and obtained n-octanal imine (57) in 32% yield (Chart 17).

Chart 17



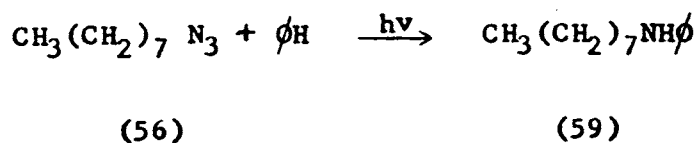
They also photolyzed n-octyl azide (56) and obtained a 45% yield of 2-n-butyl pyrrolidine (58) and 45% yield of n-octanal imine (57) (Chart 18).

Chart 18



In benzene solution they obtained a 31% yield of N-n-octylaniline (59) (Chart 19).

Chart 19



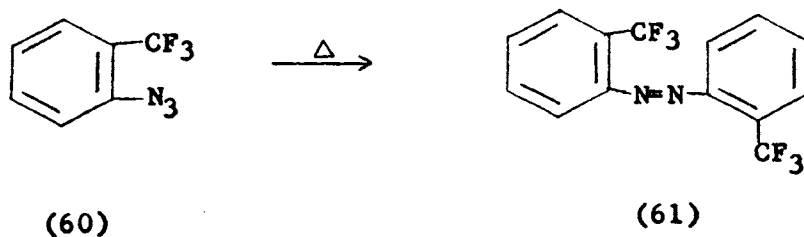
The above work with n-octyl azide was done as a model study for Barton and Morgan's synthesis of conessine.⁵⁴ However Smolinsky was unable to repeat the work and reported this to Barton. Barton

and Starrett then reinvestigated the photolysis of aliphatic azides to yield pyrrolidines. They were also unable to repeat the pyrrolidine synthesis and retracted the synthesis of conessine and aliphatic substituted pyrrolidines.⁵⁵ However they report that Moriarity (Catholic University of America, Washington, D.C.) in a personal communication informed them that he was able to repeat the pyrrolidine synthesis. This is a classic example of the difficulties associated with research in this area.

Many of the reactions which organic azides undergo have rather small energies of activation.¹⁶⁻²² With these low activation energies solvent effects appear to be very important.⁶⁷ Thus impurity in a solvent might completely change the nature of the product from an azide decomposition.⁵⁵ Also light and oxygen cause the decomposition of azides.^{4,68} Thus a reaction may not be reproducible because of a trace of oxygen being present. Products often differ when two identical azide reactions are run, one exposed to light and one in the dark.

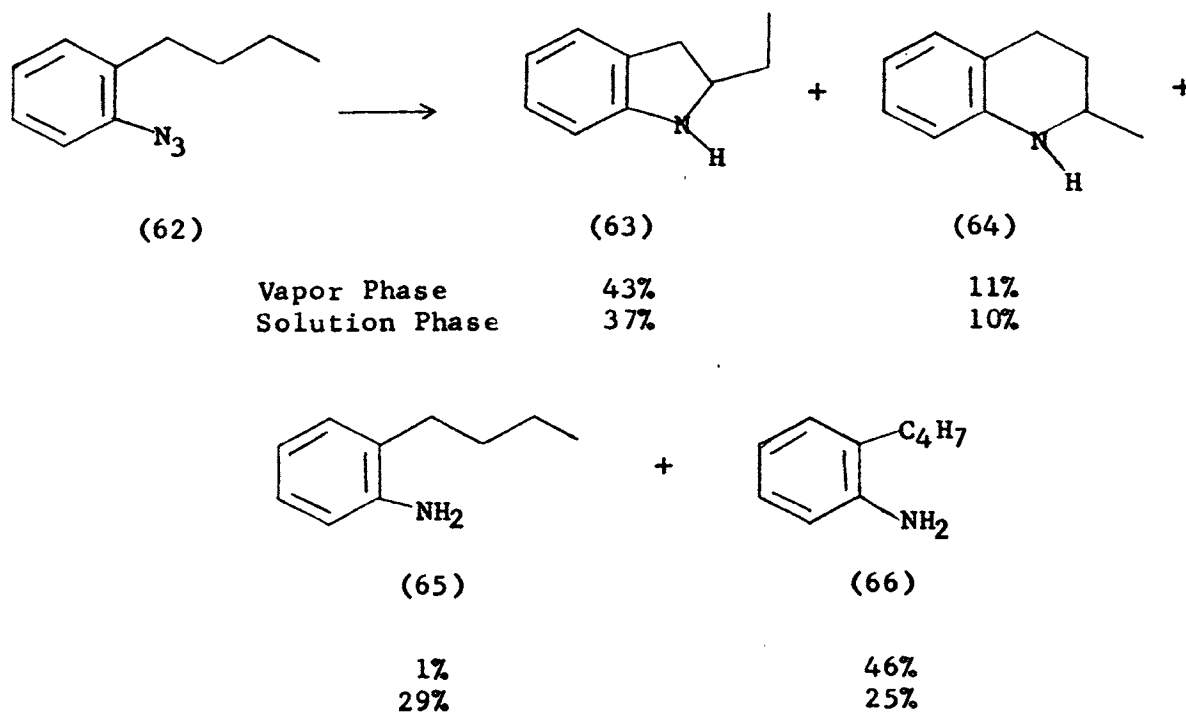
Smolinsky⁵⁶ decomposed thermally o-trifluoromethylazidobenzene (60) in the vapor phase to obtain an 80% yield of 2,2'-bis(trifluoromethyl) azobenzene (61) (Chart 20).

Chart 20



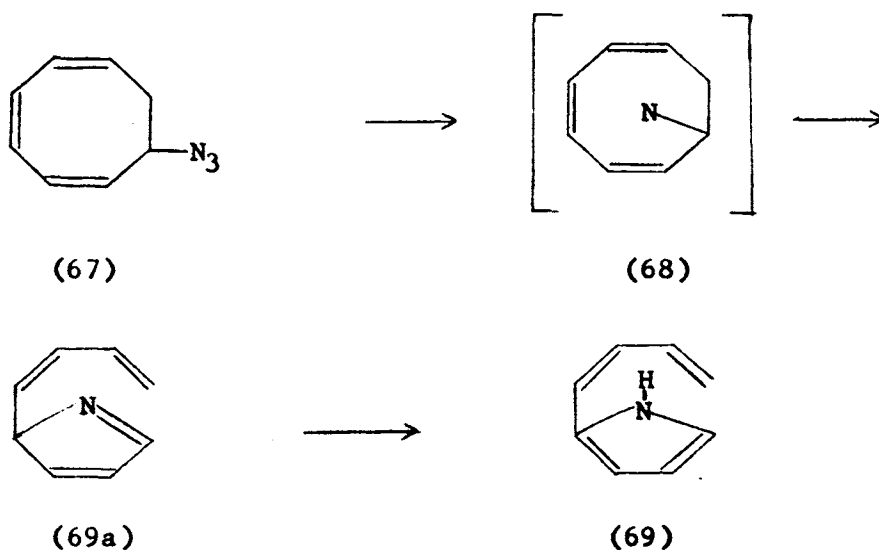
Smolinsky and Feuer⁵⁷ studied the thermal decomposition of 2-azido-n-butylbenzene (62) in both the vapor phase and in solution. They found four different products which were formed in different yields depending upon the reaction conditions (Chart 21). The products were identified by spectral and elemental analysis. The total yield was 70%.

Chart 21



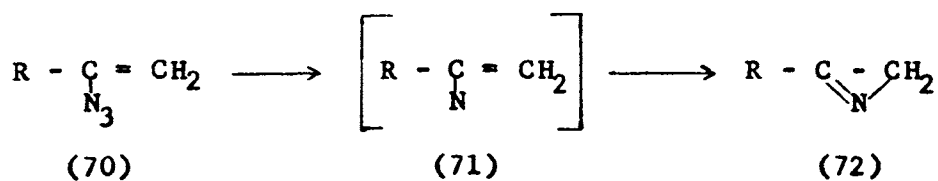
Kroner^{58,59} has reported that thermal (65°C) decomposition of the azide-substitution product of the hydrogen bromide adduct with cyclooctatetraene (67) yields a nitrene (68) which rearranges to 2-trans-butadienylpyrrole (69) (Chart 22).

Chart 22



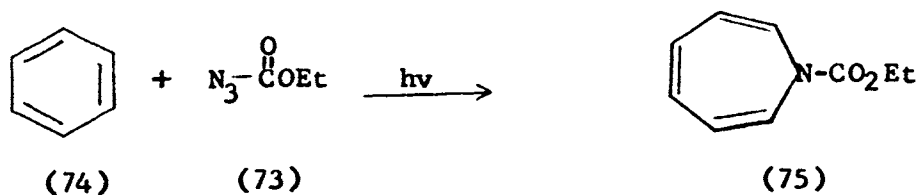
Smolinsky studied the vapor phase pyrolysis of various substituted vinyl azides.^{56,60,61} When the azide is in the 2 position aziridines are formed (Chart 23).

Chart 23



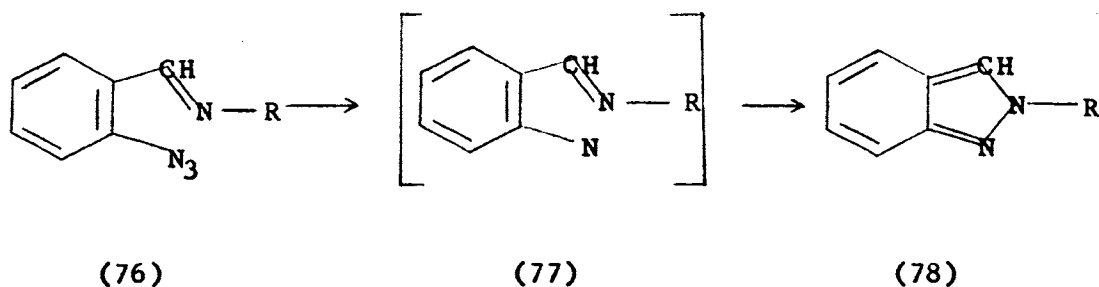
Hafner and König⁶² studied the photochemical decomposition of ethyl azidoformate (73) in benzene (74) to yield N-carbethoxyazepine (75) in 70% yield (Chart 24).

Chart 24



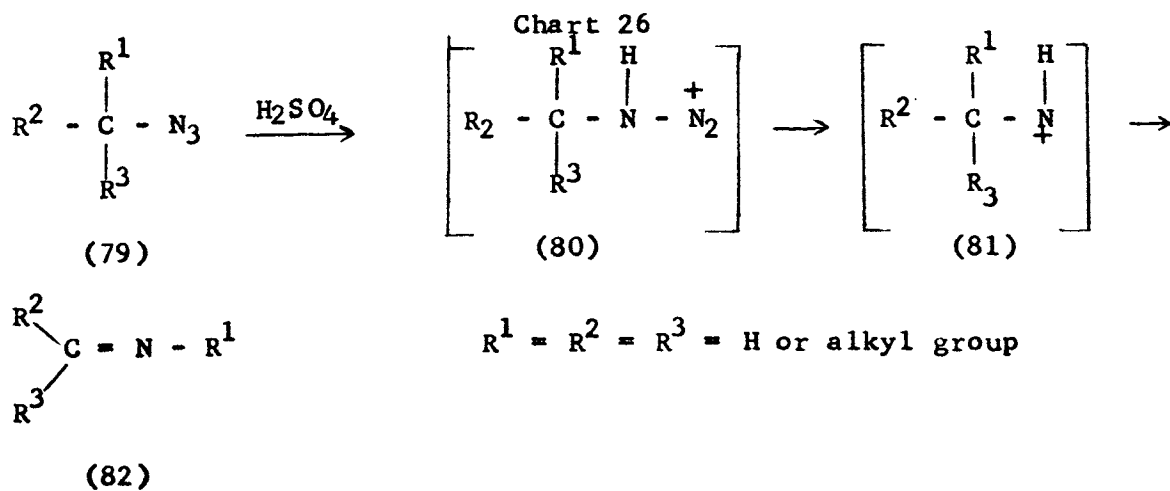
Krebechek and Takimoto decomposed thermally aryl-substituted 2-azido benzylidene amines (76).⁶³ The reaction was run in an inert solvent at 150° and goes through a nitrene intermediate (77) to yield a 5-membered ring compound (78) in 90% yield (Chart 25).

Chart 25



E. Azides As Nucleophiles

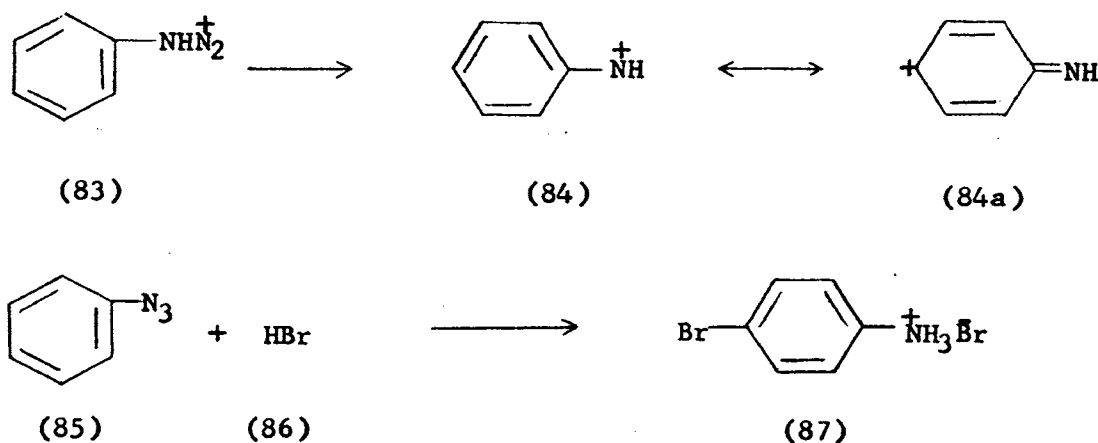
Organic azides may serve as nucleophiles and react with electrophiles. The only important reactions of this type are the reactions of azides with strong acids.⁶⁴ Alkyl azides react with concentrated sulfuric acid at room temperature to give quantitative loss of nitrogen and migration (Chart 26) of a hydrogen or alkyl group yielding an aldimine or ketimine.



In the case of vinyl azides the aldimine will rearrange further to yield a nitrile.⁶⁵

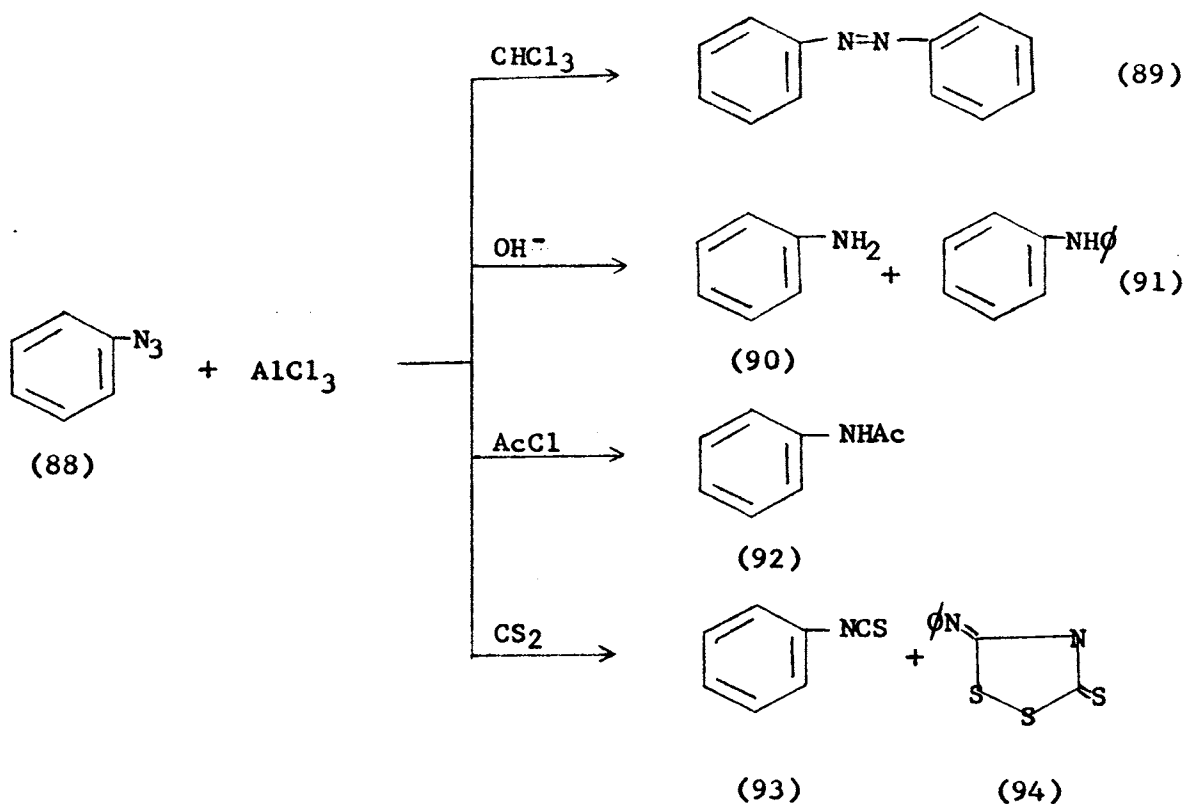
Aryl azides form several different products. Usually they react with the acid anion or with the solvent to form substituted anilines.⁶⁶ It appears that the reaction path (Chart 27) goes through the protonated azide. The nitrogen molecule may be displaced from the substituted nitrogen or the nitrogen molecule may be lost in a unimolecular process.

Chart 27



Lewis acids also react with azides. The products vary somewhat and are usually a function of the solvent.⁶⁷ The products formed from phenyl azide are shown in Chart 28.

Chart 28



F. 7-Azidotropylidene

Cycloheptatrienyl (troyl) azide was first prepared by Wulfman, Yarnell, and Wulfman.⁶⁸ It is a clear colorless liquid boiling at 50° at 2 mm. It is both oxygen and temperature sensitive. A sample left open to air at room temperature overnight will turn black. The resulting impure troyl azide may be purified by vacuum distillation. Troyl azide has typical troylidene-type infrared, ultraviolet, and NMR spectra.

A 10% solution of troyl azide in d_6 -acetone shows a temperature-dependent NMR spectrum.¹ At -35° the spectrum is very similar to that of troyl azide in carbon tetrachloride or carbon disulfide at room temperature. At -15° spin-spin splitting disappears. At 30° the chemical shifts disappear and the spectrum consists of a single broad peak 0.87 ppm wide at half height. This peak has the same center of gravity as the standard spectrum of troyl azide. In 90% d_6 -acetone 10% D_2O at 52° the peak has a width at half height of 0.45 ppm. The free energy of activation of the process occurring is 15 ± 2 kcal. Similar results are obtained in the solvent systems dimethyl carbonate, dioxane, and dioxane/ D_2O . These observations were explained by assuming the formation of an ion pair of low stability in the solvent cage and dissociation of this complex in solvents of high ionizing power.¹

Troyl azide has been used by Looker⁴ for the formation of triazoles by 1,3 dipolar additions to substituted acetylenes.

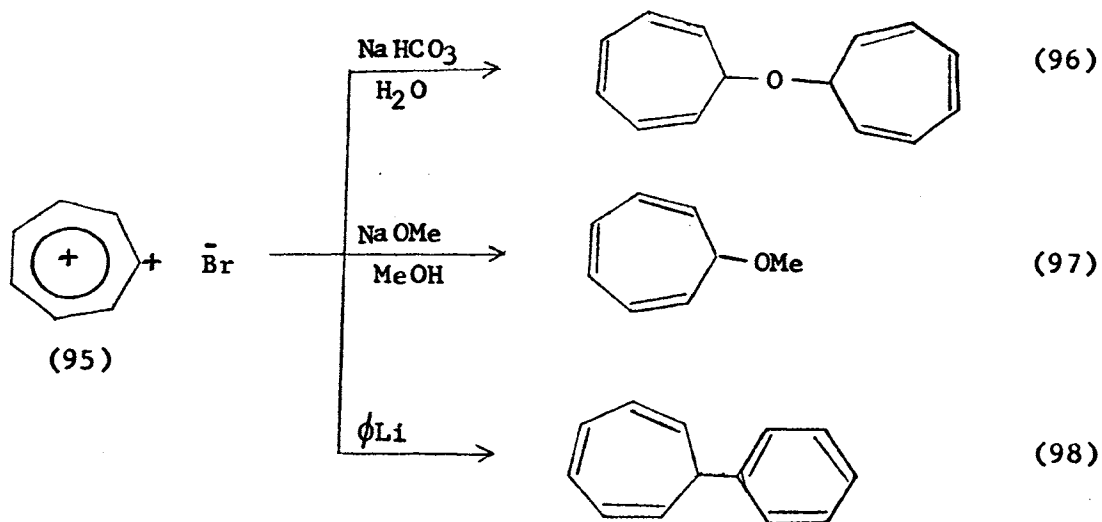
McCullagh, Wulfman, Fennessey, and Wilson⁶⁹ have shown that troyl azide can be converted into tropone on Fisher A-540 Alumina.

G. Nucleophilic Attack on Tropylium Ion to Furnish Covalent Derivatives

The cycloheptatrienyl cation (tropylium ion) was first prepared by Merling in 1898.⁷⁰ He did not realize that it was an organic compound and discarded it. Doering and Knox⁷¹ recognized that Merling had actually had tropylium ion in hand and repeated his work in 1954. This material had properties which fully supported the predictions made by Huckel⁷² in 1931. Doering and Knox⁷¹ treated tropylium ion

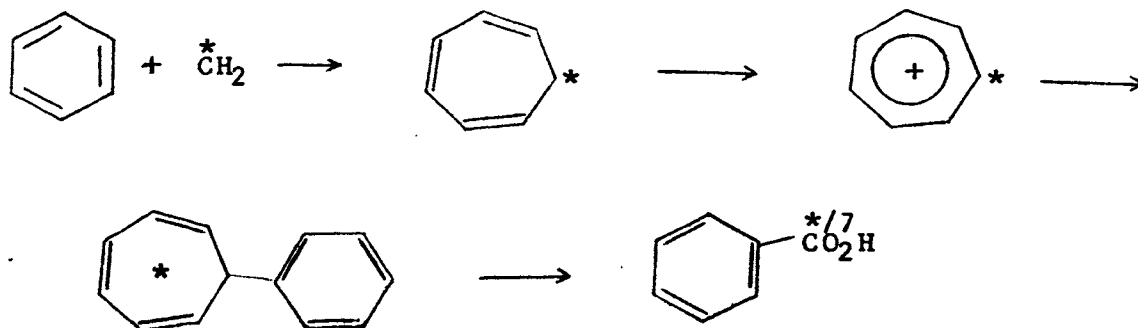
(95) with basic aqueous solutions, a solution of sodium methoxide in methanol, and phenyl lithium and obtained ditropyl ether (96), tropylium methyl ether (97), and phenyl tropylium (98) (Chart 29).

Chart 29



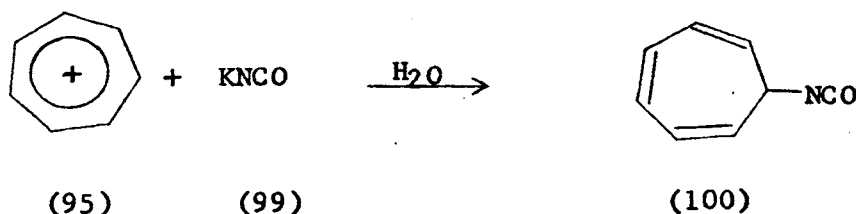
Studies by Kursanov and coworkers on ^{14}C -labeled tropylium ion (Chart 30) clearly established the equivalence of all carbons.¹⁰⁷ In contrast, the covalent derivatives of tropylium ion almost invariably exhibit C_2 symmetry and not D_{7h} . The only reported exception to this rule is tropylium azide (*vide infra*).¹

Chart 30



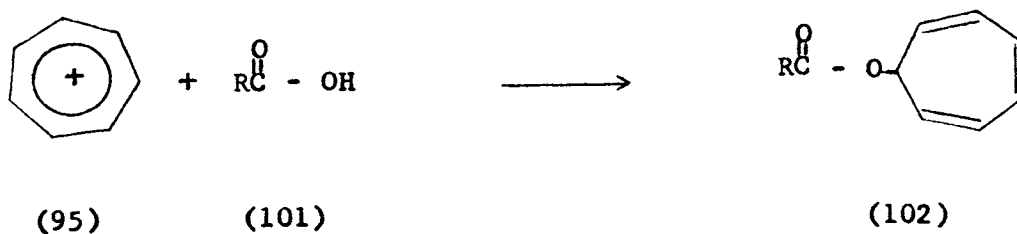
Dewar and Pettit⁷³ reported that aqueous solutions of potassium isocyanate (99) react with tropylium ion (95) to yield tropylium isocyanate (100) (Chart 31). They also reported that under special conditions they obtained a crystalline material they identified as tropylium isocyanate. This latter observation was shown to be incorrect by the Wulfmans⁶⁸ and Doering and Helgen.⁷⁴ The crystalline material proved to be ditropylium urea.

Chart 31



The Russian workers, Vol'pin, Akhrem, and Kursanov,⁷⁵ found that tropylium ion (95) reacts with carboxylic acids (101) to yield tropylium esters (102) (Chart 32).

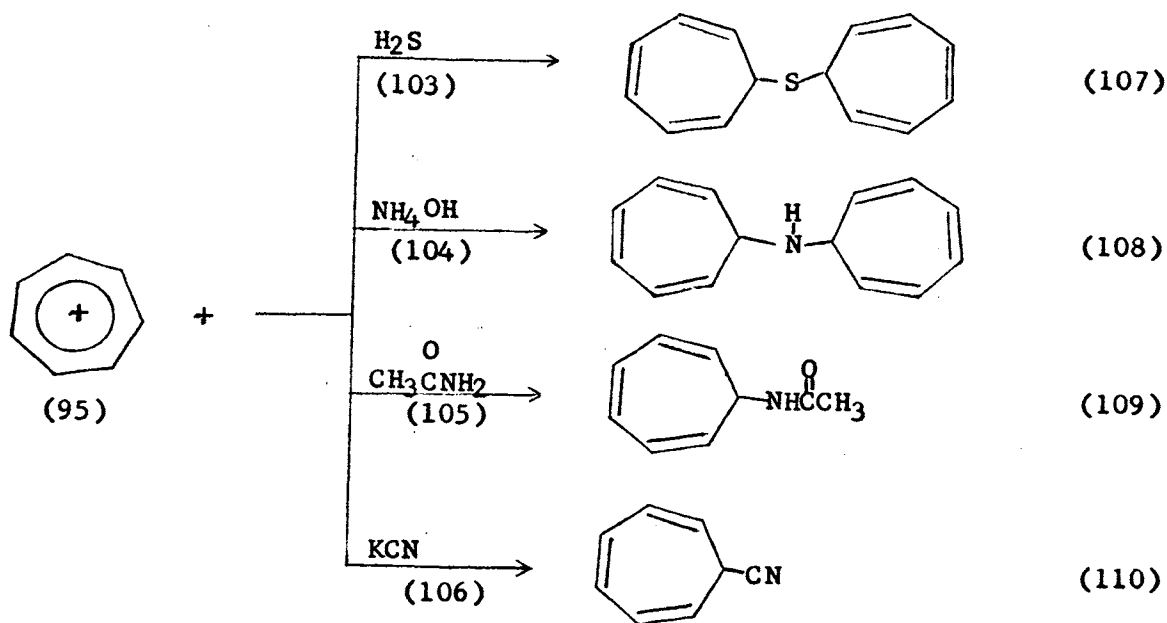
Chart 32



Doering and Knox⁷⁶ reported further on the reactions of tropylium ion with nucleophiles. They reacted tropylium ion (95) with hydrogen sulfide (103), ammonium hydroxide (104), acetamide (105), and potassium cyanide (106) and obtained respectively, ditropylium

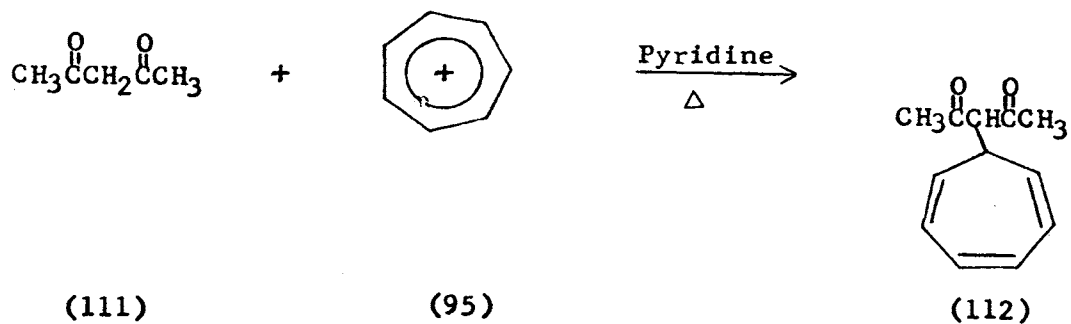
sulfide (107), ditropyl amine (108), N-tropylacetamide (109), and troyl cyanide (110) (Chart 33).

Chart 33



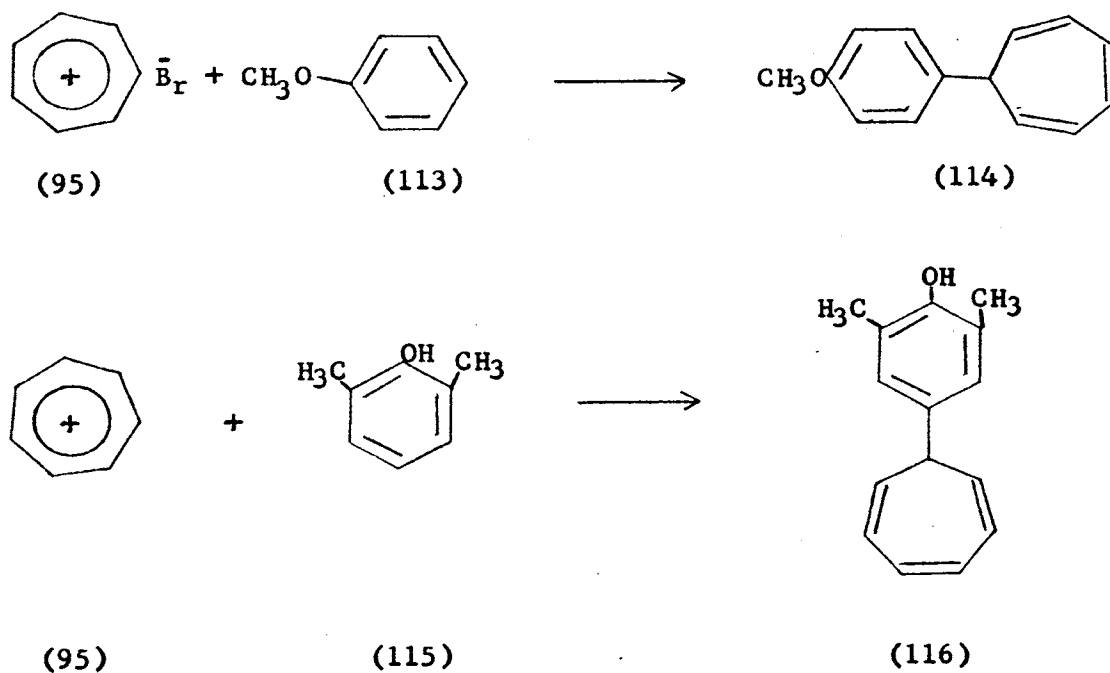
Conrow⁷⁷ reported that tropylium ion reacts with methylene compounds in the presence of a base (Chart 34) usually in high yield.

Chart 34



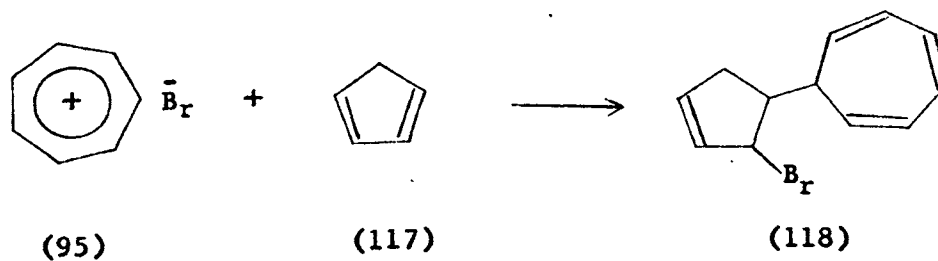
Bryce-Smith and Perkins,⁷⁸ as well as ter Borg and coworkers,⁷⁹ reported that tropylium ion (95) reacts with suitably activated aromatic compounds to yield aromatic substitution products (Chart 35).

Chart 35



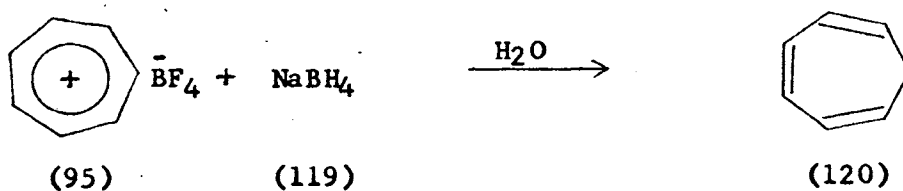
Kursanov and coworkers⁸⁰ observed that tropylium ion (95) can add to unactivated double bonds (Chart 36).

Chart 36



Muller and Fricke⁸¹ reported that tropylium ion (95) reacts with aqueous solutions of sodium borohydride (119) to yield tropyliene (120) (Chart 37).

Chart 37



III. RESULTS AND DISCUSSION

A. Tropyl Azide Work

The tropyl azide prepared by D. S. Wulfman¹ exhibited an extra peak at τ 4.34 in the NMR spectrum. This peak was insensitive to temperature and showed no structure. No adequate explanation was advanced for its cause.

One possible explanation for the extra peak in the NMR spectrum of tropyl azide was a sandwich-type system with π bonding. A system of this type could be formed from a species having a divalent negative charge to neutralize the positive charges of the two tropylium ions, and higher orbitals capable of interacting with the π systems of the tropylium ions. To see if the f orbitals of selenium or tellurium might overlap with the π system of tropylium ion we set out to make ditropyl selenide and ditropyl telluride. It was thought that the preparation of these materials would lead to sandwich structures if such structures were possible. This work was carried out by the author as an undergraduate research project. A tabulation of experimental procedures and results is listed in Appendix I. Both systems had covalent bonds and were typical tropyl systems, exhibiting chemical shifts for the 7-proton proportional to the electronegativity of the substituent.

It was relayed to us that organic azides often decompose during infrared spectrophotometric analysis.¹⁰⁰ This information led us to the speculation that, since infrared heat lamps were used in the distillation of the original tropyl azide, perhaps a thermal decomposition

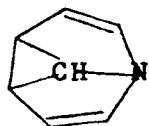
product of troyl azide was responsible for the extra peak in the NMR spectrum.

It is possible to write a number of structures for products that might result from the decomposition of troyl azide (Chart 1) in excess troyl azide, allowing for 1,3 dipolar additions, with or without subsequent loss of nitrogen, nitrene reactions and their valence isomers and also possible further interactions with troyl azide.

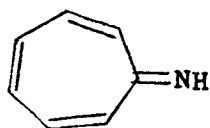
Chart 1



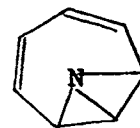
(1)



(2)

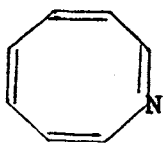


(3)

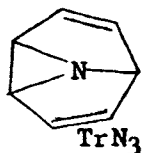


(4)

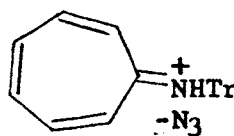
Tr = 7-cycloheptatrienyl



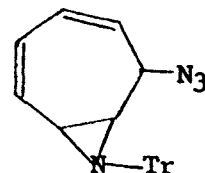
(5)



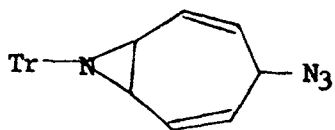
(6)



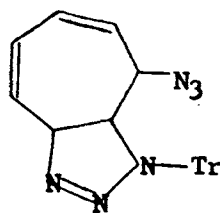
(7)



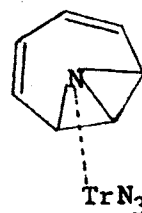
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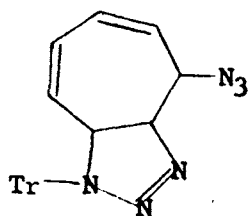
(9)



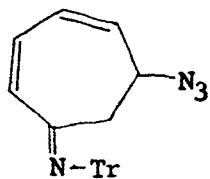
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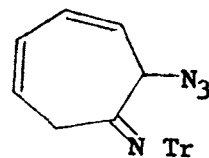
(11)



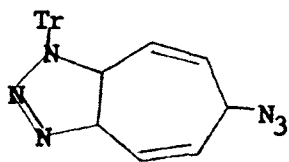
(12)



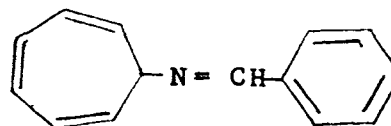
(13)



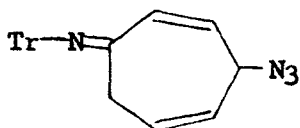
(14)



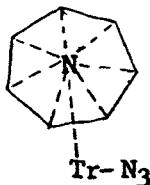
(15)



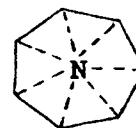
(16)



(17)



(18)



(19)

Of these possible products, only three related compounds have now been reported in the literature. The fluoborate salt of compound (3) has been reported by Bauld,⁸⁶ and the fluoborate salt of compound (7) has been reported by Dauben and coworkers.⁸⁷ The 2-methoxy substituted form of compound (5) has been reported by Paquette and Phillips.⁹¹

Compound (19) was viewed as a π -bonded system with the nitrogen atom above the plane of the ring and equally bonded to all seven carbons. Extended Huckel and simple Huckel molecular orbital calculations

were performed on structure (19) by D. S. Wulfman, D. W. Beistel, and C. E. Wulfman.¹⁰⁴ Correlation diagrams for the system are shown in Appendix V. These diagrams show that compound (19) is symmetry allowed and that there will be a net gain in the π energy in excess of that associated with the localized bonded compound 1 aza-tricyclo (3,3,0,0)^{1,8} octa-3,6-diene. The diagrams encompass the range of values normally employed for the integral α and β for CHN compounds.

The photolysis of troyl azide in the vapor phase with ultraviolet irradiation yielded only black intractable tars. Liquid-phase photolysis also furnished a black intractable mixture. An infrared thermolysis of troyl azide was run in the vapor phase. This procedure was carried out by distilling troyl azide through a Vycor tube irradiated with infrared sun lamps at pressures lower than 3mm. At pressures above 3 mm the reaction tended to flash into the pot. The distillate (white solid in pale yellow troyl azide) was collected on a liquid nitrogen cold finger. The white solid was isolated by trituration with hexane and was oxygen- and heat-sensitive. The yield at this point was usually 10 to 50 mg per 10 ml of troyl azide.

The IR spectrum of the white solid in methylene chloride showed an azide peak at 4.74 μ . This corresponds to a partially ionic azide.^{27,28} The UV spectrum had $\lambda_{\text{max}}^{\text{EtOH}}$ 236 nm (ϵ 10,000), 238 nm (ϵ 10,000), 240 nm (ϵ 10,000), 247 nm (ϵ 8,000), 287 nm (ϵ 2,000), 317 nm (ϵ 5,000), 325 nm (ϵ 5,000).

The NMR spectrum of the white solid in acetonitrile displayed a broad peak centered at τ 2.4 (6H), a triplet at τ 3.2 (2H), a quartet at τ 3.6 (2H), a quartet at τ 4.4 (2H), and a triplet at τ 6.0 (1H). Upon treatment with trifluoroacetic acid it displayed

the same broad peak at one half the original intensity plus a peak of equal intensity at τ 0.7 (tropylium ion).

Atmospheric pressure hydrogenation of the white solid yielded cycloheptylamine, cycloheptane, and 3-aminocycloheptene. These compounds were identified by mass spectral analysis. Authentic samples were synthesized and used as comparisons.

A determination of the azide concentration of the white solid gave a value of $20\% \pm 2\%$. The theoretical value for compound (7) is 17.65%. A colorimetric analysis was used. The inaccuracy of the method plus the difficulty of removing the last traces of troyl azide from the solid account for the apparently high azide concentration.

These facts are suggestive of structure (7) in Chart I for the white solid. Dauben and coworkers⁸⁷ have prepared the fluoborate salt of compound (7). They found the following properties for this salt. The NMR spectrum in acetonitrile showed a multiplet at τ 2.35 (6H), a triplet at τ 3.15 (2H), a quartet at τ 3.56 (2H), a quartet at τ 4.42 (2H) and a triplet at τ 6.00 (1H).

The UV spectrum showed two peaks at 240 nm and 330 nm. Extinction coefficients and infrared spectral data were not given. The fluoborate salt melts at 109° and readily loses tropylium ion in the presence of an acid (ethanol) to form tropone imine fluoboric acid salt. The fluoborate salt of compound (7) is oxygen and heat sensitive.

The white solid's similarity in the UV and NMR spectra to tropone imine compounds,^{86,87} and the fact that it yields a tropone immonium salt plus tropylium ion upon treatment with acid, (as suggested by NMR studies) and the fact that it contains $20\% \pm 2\%$ ionic azide

led us to the conclusion that it was N-tropyl tropone-imine hydrazoic acid salt.

It was also observed that if tropyl azide (10 g) was irradiated and then stored under nitrogen in a freezer at -20° , a crystalline pale yellow solid (150 mg) precipitated after about 48 hours. This material was insoluble in everything except very polar solvents, and strong acids. Its NMR spectrum in d_3 -nitro-methane showed a narrow multiplet centered at τ 2.4.

It was also found that when freshly prepared, clear, colorless tropyl azide under nitrogen was stored at -20°C for ten days the same yellow solid was formed. The yield averaged 150 milligrams per 10 g of tropyl azide. The residual tropyl azide was a reddish brown liquid and contained about 4% brown amorphous material which was left behind upon vacuum distillation. No attempt was made to characterize the brown material.

Looker⁴ has reported that tropyl azide left at room temperature for several hours turned dark and a crystalline material precipitated but he discarded the material at that time without attempting to identify it.

The crystals we isolated darkened at $88-90^{\circ}$ and melted at $140-143^{\circ}$. An IR (nujol mull) spectrum showed peaks at $4.9\ \mu$ (m) (N_3), $6.1\ \mu$ (w) ($\text{C}=\text{C}$), $6.65\ \mu$ (m), $6.7\ \mu$ (m) ($\text{C}=\text{C}$ or $\text{C}=\text{N}$), $8.0\ \mu$ (w) and $12.8\ \mu$ (m). The UV spectrum show $\lambda_{\text{max}}^{\text{EtOH}}$ 236 nm, 316 nm (sh), and 325 nm. The percentage of azide ion was $26\% \pm 2\%$. The theoretical amount for $\text{C}_7\text{H}_8\text{N}_4$ was 28.2%. These crystals upon treatment with fluoboric acid in acetonitrile and ether precipitation yielded the fluoborate salt of

tropone imine. The melting point and mixed melting point with an authentic sample was 193-195° (lit⁸⁷ mp 188-192°).

Dauben and Rhoades⁸⁷ have prepared the fluoborate salt of compound (3) in Chart 1. They list the following properties for the salt.⁸⁷ The NMR spectrum in acetonitrile shows a sharp multiplet at τ 2.35. The UV spectrum shows $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 234 nm, 315 nm (sh), and 324 nm. Extinction coefficients were not given. The IR spectral characteristics were not given either. The melting point is 188-192°. The salt is described as white plates.

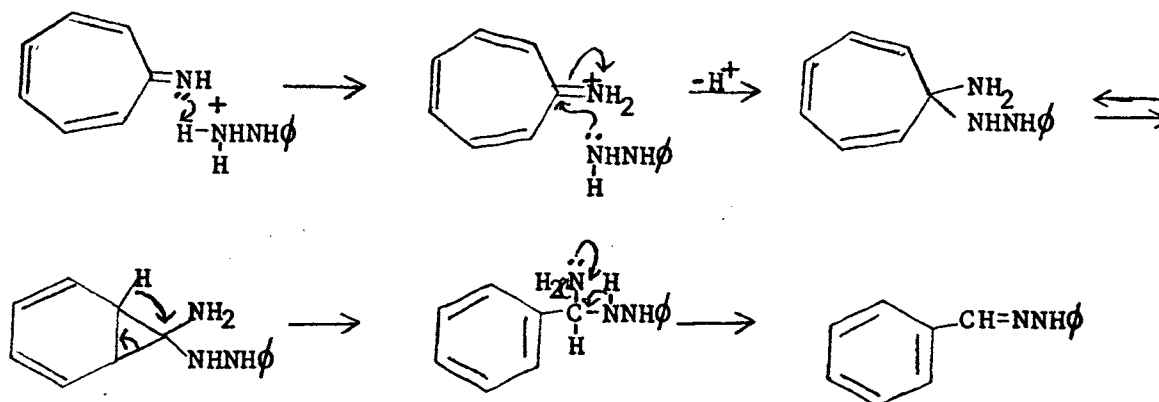
The conversions of the yellow solid to tropone imine fluoboric acid salt, the ionic azide percentage composition, and its similarity in the NMR and UV spectra to tropone imine fluoboric acid salt suggest that the white solid is tropone imine hydrazoic acid salt.

The above reactions appear to be the first preparation of either azide salt.

To check the possibility that compounds (4) and (11) and their expected rearrangement products: benzaldimine and (16) might be present, the yellow solid was treated with dinitrophenylhydrazine reagent. On the basis of precedents in these laboratories and at Oregon,¹⁰⁶ compounds (4) and (11) would be expected to undergo facile rearrangement to the benzaldimine systems. This derivative does form after about 10 minutes. It was identified by melting point and mixed melting point as the dinitrophenylhydrazone of benzaldehyde. However when the same test was performed on authentic samples of tropone-imine similar results were obtained.

The formation of the dinitrophenylhydrazone of benzaldehyde from tropone imine at first appears strange. We propose the mechanism shown in Chart 2.

Chart 2

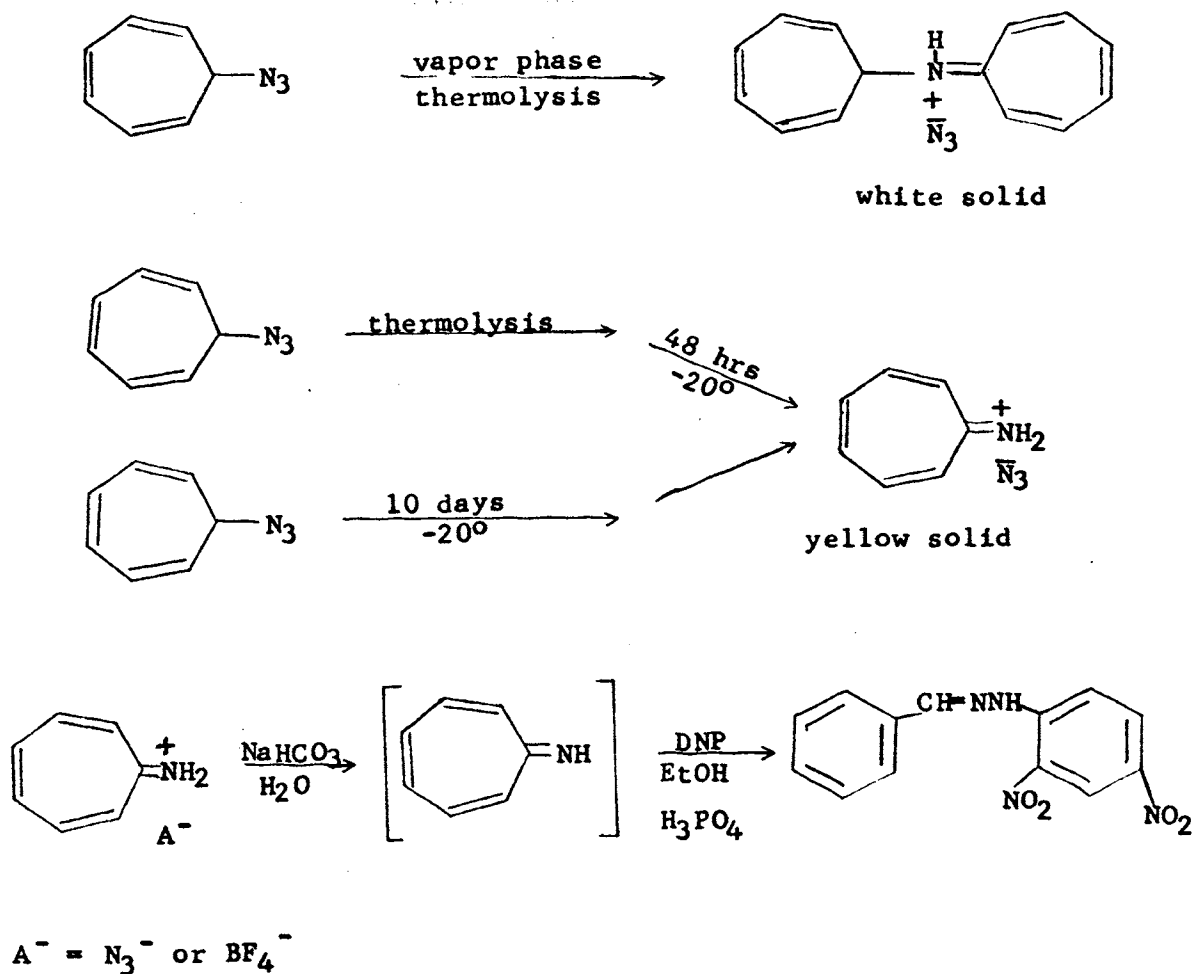


Nozoe¹⁰⁵ has succeeded in preparing a number of tropone-imine type derivatives from tropones using standard reagents for forming carbonyl derivatives. His synthesis of the dinitrophenylhydrazone of tropone was realized via tropone-oxime. From the reported properties it is evident that the compound is not benzaldehyde dinitrophenylhydrazone. The data reported on other tropones are clearly inconsistent with the expected rearrangement products. This suggests that we have observed a new rearrangement in the tropone-imine series. Similar rearrangements have been observed under oxidizing conditions in both acidic and basic media with tropylidenes, tropones, and tropylium ion.^{76, 102}

A number of reactions were observed which were not reproducible. They will not be discussed here; however, they appear in Appendix III

of this thesis. The isolation of the compound listed in the publication in Appendix II was not found to be reproducible. There are sufficient differences in the properties of this compound and the tropono-imines to suggest that the materials are not one and the same.

A flow sheet of the reactions observed is given here to summarize this section.



B. Reactions of Tropylium Ion With Nucleophiles

1. Interaction of Tropylium Ion With Tertiary Amines

The addition of nucleophiles to tropylium ion was the subject of a Ph.D. Thesis at Yale University by P. B. Shevlin.⁹⁴ He studied the reaction of tropylium fluoborate with various tertiary amines and reported that tropylium fluoborate reacted with an equivalent amount of pyridine in acetone to give an NMR spectrum showing the pyridinium protons as a complex multiplet between τ 1.5 and 2.2, and the troyl protons as a single peak at τ 3.4. Since he felt the reaction should yield N-troylpyridinium fluoborate, he rationalized the single peak by postulating a rapid equilibrium between pyridine, tropylium ion and N-troyl pyridinium fluoborate. He claimed the theory was proven by the NMR spectrum of the reaction at -20° which showed a complex multiplet for the troyl protons. He felt that this showed the equilibrium existed and was slower at -20° .

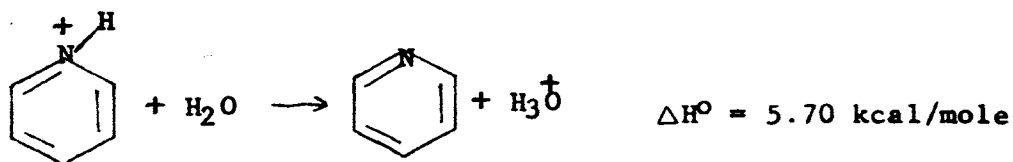
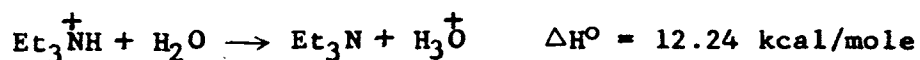
However, when triethylamine was employed as the base, a somewhat different spectrum was obtained. The spectrum showed a quartet centered at τ 6.8 and a triplet centered at τ 8.7 for the ethyl groups and a typical troyl spectrum with a broad singlet at τ 3.3 (2H), a broad doublet centered at τ 3.9 (2H), a multiplet centered at τ 4.7 (2H), and a well-resolved triplet centered at τ 5.9 (1H). This result was explained by postulating that the N-troyltriethylammonium fluoborate was formed, but did not dissociate fast enough to show up as a single peak.

Spectra of typical troyl compounds were also obtained with tributylamine, 2-picoline, or 2,4-lutidine as the base.

He further reported that the position of the peak at τ 3.4 is a function of the ratio of the concentrations of tropylium ion and pyridine. Excess tropylium ion results in a downfield shift of the peak.

He then narrowed his study down to two of these combinations. He measured the ΔH° of dissociation of N-tropylpyridinium fluoborate and N-tropyltriethylammonium fluoborate with ultraviolet spectroscopy measurements. From these he determined that $\Delta H^\circ = 7.00$ kcal/mole for dissociation of N-tropylpyridinium fluoborate and that $\Delta H^\circ = 13.75$ kcal/mole for dissociation of N-tropyltriethylammonium fluoborate. He attributes the difference to the difference in basicity of pyridine and triethylamine using the following equations^{95,96} (Chart 3).

Chart 3



He stated that the difference in ΔH° for the reaction of the amines with tropylium ion was 6.75 kcal/mole. This was quite close to the value of the difference of 6.54 kcal/mole between the reactions shown in Chart 2. He assumed that the basicity of the amines toward a carbonium ion and a proton were the same and that the basicity of the amines explained the difference in ΔH° of dissociation for the tropylium ion-amine salts.

We became interested in this type of work as a sidelight in the study of troyl azide decomposition products and discovered the same phenomenon independently. Our original work was done using acetonitrile as the solvent. We found that triethylamine and troylium perchlorate in acetonitrile gave a typical troyl spectrum. We also found that pyridine and troylium perchlorate in acetonitrile gave a single troyl peak at τ 3.4.

Calorimetric studies of the system triethylamine-troylium perchlorate in acetonitrile were conducted by Professor Bertrand of our department.⁴⁰ In one experiment where the ratio of troylium ion to triethylamine was 1:1, a heat of 15 kcal/mole of troylium ion was evolved. In another experiment with a ratio of troylium ion to triethylamine of 1:2, 30 kcal/mole of troylium ion was evolved. A third experiment with a ratio of troylium ion to triethylamine of 1:10, could be interpreted as the evolution of about 30 kcal/mole of troylium ion in conjunction with a slower endothermic process.⁵

The above results indicate that the reaction of troylium ion with triethylamine is quite complex. The heat of reaction appears to be dependent upon the ratio of the two reactants. It would appear that at least three processes can occur depending upon the ratio of the reactants (eg., formation of 1:1 and 1:2 complexes and oxidation of the complexes by troylium ion). In a large excess of triethylamine the endothermic reaction may be due to exchange of alkyl groups between triethylammonium ions and triethylamine as found for other quaternary ammonium ion salts,⁹⁷ as well as oxidation-reduction processes, as reported by McGeachin.¹⁰⁸

Shevlin pursued the study further by preparing ca 98% perdeuterated tropylium ion and determining the variable-temperature NMR spectra of the ion and pyridine in acetone, dimethyl sulfoxide, and acetonitrile. He found that the troyl peak was very temperature sensitive. The deuterium content of the tropylium ion was high and thus the spectra showed no spin-spin splitting at low temperatures. He reports that the single peak at τ 3.4 at room temperature splits into a doublet at -12° and into a quartet with ratios 2:2:2:1 at -55° to show a well-resolved troyl spectrum. The positions of these peaks are separated by a total of 41.7 Hz. He defined the locations by setting the α protons equal to zero. Thus the positions are as follows: $H_{C_7} = 4.2$ Hz, $H_\gamma = 0$, $H_\beta = -28.0$ Hz, and $H_\alpha = -37.5$ Hz. He calculated the Arrhenius energy of activation for the dissociation of N-tropyropyridinium fluoborate in the three solvents mentioned. These parameters are as follows: acetone, $E_a = 4.83$ kcal/mole, dimethylsulfoxide, $E_a = 10.6$ kcal/mole, and acetonitrile, $E_a = 16.0$ kcal/mole. However the ΔS^\ddagger for the reaction changes in the following order: acetone $\Delta S^\ddagger = -30.3$ e.u., dimethylsulfoxide $\Delta S^\ddagger = -12.5$ e.u., and acetonitrile $\Delta S^\ddagger = -6.5$ e.u. This leads to a nearly constant rate of dissociation of the N-tropyropyridinium fluoborate in the three solvents.

There appeared to be several discrepancies in the work of Shevlin. First, it has been reported that tropylium ion reacts with dimethylsulfoxide to yield the same type of salt as amines do.¹ Secondly, the supposed spectrum of N-tropyropyridinium fluoborate at -55° has only a 41.7 Hz spread whereas any troyl system will be

spread over at least 70 Hz not counting the location of the γ proton which is proportional to the electronegativity of the γ substituent (Table 1).

Table 1

NMR Spectra of Tropyli Compounds

Compound	Position of Peaks in τ Units			
	$H_{C\gamma}$	H_{α}	H_{β}	H_{γ}
Tr- γ -C ₇ H ₇				
TrOAc	4.89	4.53	3.88	3.35
TrOMe	6.83	4.63	3.95	3.42
Tr--Me	8.75	5.30	4.20	3.67
Tr--H	7.80	4.72	3.88	3.45
Tr ₂ NH	7.08	4.70	3.93	3.40
Tr ⁺ NEt ₃ BF ₄ ⁹⁴	5.95	4.63	3.89	3.34
Tr ₂ Sc	6.92	4.67	4.00	3.50
Tr ₂ Te	7.10	4.67	4.00	3.50
Tr-t-C ₄ H ₉	8.93	4.79	3.97	3.40
Average		4.74	3.97	3.44

The average distance between H_{α} and H_{γ} for the above compounds is 1.3 τ units which is equal to the 78 Hz at 60 MHz.

Therefore we decided to investigate this matter more fully. A 10% solution of tropylium perchlorate in d₅-pyridine was prepared. This solution had a light yellow color. Variable-temperature NMR

spectra were determined for this solution; the single peak at τ 3.4 broadened down to -20° . At -30° it split into a doublet and remained a well-resolved doublet down to -70° . The distance between the two peaks was 22 Hz. There was never any indication of a quartet. Some of this sample was dissolved in acetone and the variable-temperature NMR spectra of the acetone solution recorded. The doublet was split by 35 Hz in acetone solution. These spectra are shown in Figures 1 through 10.

The line widths of the spectra shown in Figures 1 through 10 were measured. From these the activation for the exchange process was calculated. The line broadening was of about the same magnitude as that reported by Shevlin. We used the formula below for calculating the rate.^{99*}

$$R = \frac{\pi}{2} \frac{\Delta^2}{\sigma - \sigma^0}$$

Δ = distance between peaks in absence of exchange

σ = width of peak at half height at any temperature

σ^0 = natural width of peak

The log of the rate was then plotted against the reciprocal of the absolute temperature and the slope measured. The following equation was used to calculate E_a .

$$\text{slope} = \frac{0.4343 E_a}{R}$$

The activation energy, E_a , from these measurements, for tropylium ion in d_5 -pyridine, is 8.4 kcal/mole, and in acetone solution $E_a = 4.6$ kcal/mole. Shevlin obtained values varying from 4.8 to 16.6 kcal/mole depending upon the solvent.

*For multiproton processes this is a good first approximation.

A 10% solution of tropylium perchlorate in dimethylsulfoxide was prepared. It showed tropylium ion plus a typical troyl spectrum after 10 minutes. The troyl spectrum intensity continued to increase at the expense of the tropylium ion peak. The solution was a brilliant yellow color. A small quantity of pyridine was added after 30 minutes. The singlet at τ 3.4 appeared but the typical troyl spectrum remained. Thus it appears that the reaction of pyridine with tropylium ion and the reaction of dimethylsulfoxide with tropylium ion are competing concurrent reactions.

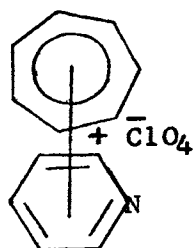
We think that Shevlin's numerical data for the most part are valid. We feel that his observation of a quartet is due to the deuterium in his samples or formation of 4 different complexes. Partially deuterated compounds often give odd splitting patterns.¹⁰⁹ Dimethylsulfoxide was a poor choice of solvent since it reacts with tropylium ion as reported by Kitahara and Funamizu,¹¹⁰ and this would certainly interfere with kinetic measurements.

We take exception to his interpretation of the data. We feel that the reaction of pyridine with tropylium ion is more complicated than merely an acid-base reaction. It would appear unlikely that the troyl protons would fall over a range of only 41 Hz when the spectrum of N-troyltriethylammonium fluoborate exhibits a typical troyl spectrum covering about 80 Hz for the α , β , and γ protons. The C_7 proton is removed from the above peaks by an additional 95 Hz. If pyridine forms a salt of the same type then the fully resolved spectrum should be very similar to that of the triethylamine salt.

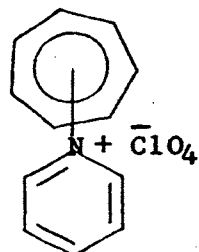
The fact that the spectra are quite different suggests the products themselves are quite different. We think that the reaction should be investigated further to determine the products and the mechanism.

The NMR spectrum of the triethylamine-tropylium ion salt is in agreement with the structural assignment. The methylene protons from the ethyl groups are shifted slightly downfield and the methyl protons do not appear to be affected by the positive nitrogen. Much more indicative of this structure, however, is the location of the C₇ proton from the troyl group. The location in this proton is very sensitive to the 7 substituent. In N-troyl-triethylammonium perchlorate in acetonitrile the C₇ proton is found at τ 5.95. This is in excellent agreement with the position of the C₇ proton in N-troyl-tropone imine fluoboric acid salt of τ 6.00 reported by Dauben and coworkers.⁸⁷

The fact that the single peak for tropylium ion in d₅-pyridine at τ 3.4, in our work, is resolved at -30° into a doublet and remains a doublet down to -80°C suggests that there are two types of tropylium ions present in solution. We like to suggest that they are an n- π bonded system and a π - π bonded system, but have no proof of this. Diagrams of these systems are shown below.



π - π Bonding



n - π Bonding

In order to shed some light upon the interactions of tropylium ion with pyridine, the interaction of several substituted pyridines with tropylium ion was investigated. The materials chosen were: 2-picoline, 2,4-lutidine, 2,6-lutidine, and 3,5-lutidine.

When 10% by weight of tropylium perchlorate was added to pyridine, it went into solution immediately to form a bright yellow solution. When 10% by weight of tropylium perchlorate was added to any of the substituted pyridines listed above, it failed to go into solution. Several of the slurries were heated to about 70°C and the tropylium ion still did not dissolve. After three hours at room temperature an NMR spectrum showed only the spectrum of the amine and no other peaks in each case.

Slurries were then prepared which were 5% by weight of tropylium perchlorate in d_6 -acetone. The various amines in an equimolar amount to the tropylium ion were then added to the slurries. Even under these circumstances the tropylium salt did not completely dissolve. Initially the spectra showed only a spectrum of the amine. After about one half hour additional peaks began to appear. The spectra of 2-picoline, 2,4-lutidine, and 2,6-lutidine show typical troyl spectra. For example, 2,6-lutidine and tropylium perchlorate in d_6 -acetone show the following peaks for the troyl protons: a multiplet at τ 3.23 (2H), a doublet at τ 3.77 (2H), a quartet at τ 4.43 (2H), and a multiplet at τ 6.30 (1H).

The 3,5-lutidine and tropylium perchlorate in d_6 -acetone showed one additional peak in the NMR spectrum after 30 minutes. The peak

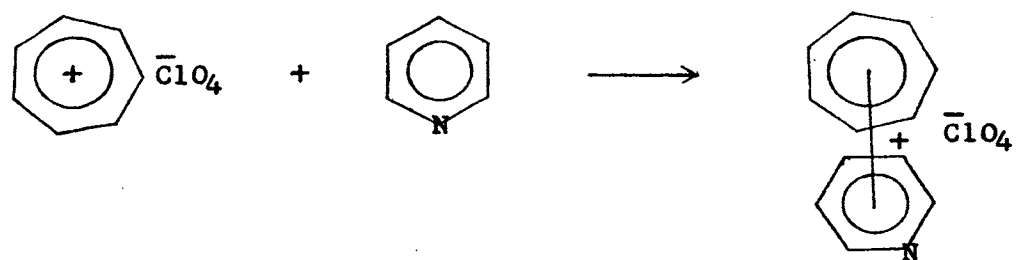
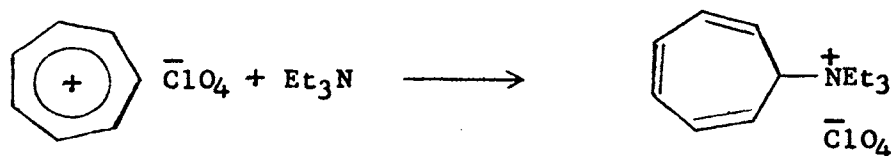
splits into a doublet separated by 20 Hz at 20°C. The peaks are in the ratio of about 3:1 with the downfield peak being the larger. At -20°C the peak has broken up into three peaks with approximate ratios 4:2:1. The largest peak is once again the downfield peak. If we assign the largest peak the number 1 and number going upfield, then $J_{12} = 44$ Hz and $J_{23} = 33$ Hz at -20°C. Integrations of the peaks proved impossible due to very small concentration of the complex and resulting lack of accuracy in the attempted integrals.

Only 3,5-lutidine appears to form a charge-transfer complex of the type formed by pyridine. The reaction is much slower with 3,5-lutidine than with pyridine. It would appear that complex formation is very sensitive to steric factors since a methyl group in the 2-position of the pyridine ring apparently prevents formation of appreciable amounts of the $n-\pi$ complex as well as the $\pi-\pi$ complexes. It would appear that at least 3 different complexes can be formed when the amine is in excess, viz. $n-\pi$, a $\pi-\pi$ and a 2 amine:1 tropylium ion $(\pi-\pi)^2$ or $\pi-\pi + n-\pi$ complex.

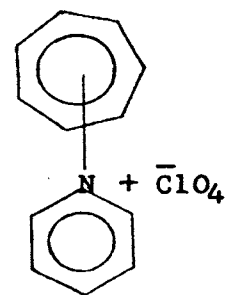
These results are somewhat surprising in light of the known behavior of charge-transfer species involving methylated benzenes and tetracyano-ethylene. In those systems, the ease of formation of complexes is facilitated by methylation and the resulting increase in π electron density results in an increase in the extent of complex formation. The introduction of methyl groups on pyridine would be expected to have similar results. That this is not the case here, suggests that considerable more study is needed on the pyridine-tropylium ion complexes using a combination of variable temperature ultraviolet-visible and nuclear magnetic resonance spectral studies

in conjunction with thermodynamic studies.

A flow sheet of our interpretations of the reaction of tropylium ion with triethylamine and pyridine is shown below.



π - π Bonding



n - π Bonding

2. Reaction of Tropylium Ion With Acetate and Substituted Acetate Anions

As a further extension of the NMR study of tropylium ion reactions with nucleophiles we attempted to prepare troyl acetate and the troyl chloroacetates. It was felt that the acetate might exist in ionizing solvents as the tropylium-acetate ion pair in analogy with the results obtained with troyl azide.¹ The chloro-substituted acetates (neat) should become progressively more ionic as the number of chlorines increases. This study should have cast considerable light upon the interaction of tropylium ion with nucleophiles by comparison of the properties of the troyl acetates with the base strength and nucleophilicity of the corresponding acetate anion.

The preparation of these compounds was attempted through a metathesis of tropylium ion with the appropriate potassium acetate salt. The results from these reactions were quite surprising.

When tropylium perchlorate was mixed with an aqueous solution of potassium acetate (which was basic) and the resulting slurry extracted with a large excess of methylene chloride, troyl acetate was obtained in 11% yield. However, tropone in 4.7% yield was also obtained. The isolation of tropone was quite unexpected and appeared to be without precedent. These compounds were isolated by removal of the methylene chloride at reduced pressure and vacuum distillation of the residue. The acetate was identified by its IR, UV, and NMR spectral characteristics. The tropone was identified by its boiling point and characteristic UV and NMR spectra.

The same reaction was carried out with tropylium ion and potassium chloroacetate.

Tropone, in 25% yield, and tropyliene, in 14% yield, were isolated. These were identified by boiling point and spectral characteristics. In a system where a 3% yield could have been detected no tropyliene chloroacetate could be found.

Through the use of UV and NMR spectroscopy the tropylium perchlorate was found to contain no detectable amounts of tropone or tropyliene. The limit of such an analysis is less than 3 percent. Since the solid salt was precipitated from aqueous acidic solution in which tropone is quite soluble, and washed with large excesses of ethanol and diethyl ether in which tropyliene is infinitely soluble, the tropylium perchlorate would be expected to contain far less than 1% of either compound.

It was thought that perhaps the basic solution present led to the formation of ditropyl ether and this subsequently decomposed to tropone plus tropyliene. To test this hypothesis we mixed potassium chloroacetate and tropylium perchlorate in very dry acetonitrile and stirred the slurry at room temperature for 30 minutes. The slurry was then filtered and the acetonitrile removed at room temperature at aspirator pressure. The liquid residue was then vacuum distilled. The only product isolated (in 31% overall yield) was tropone.

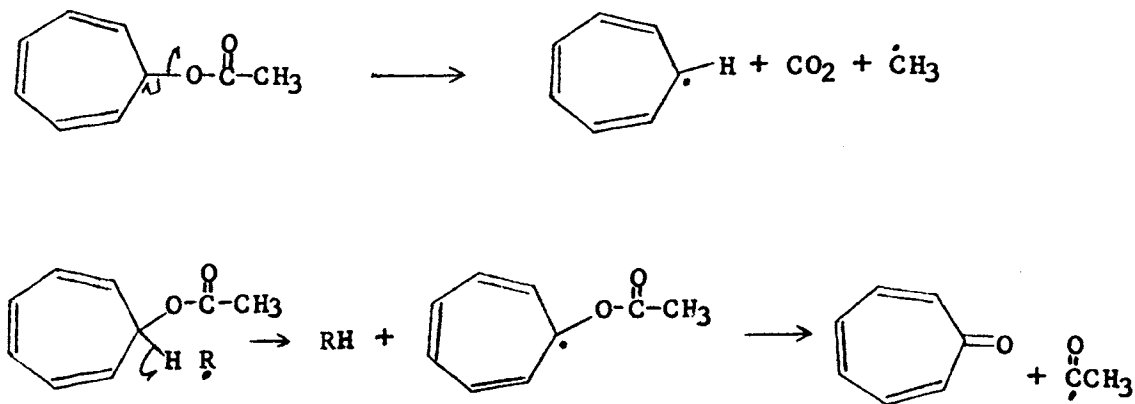
The reaction in aqueous phase was repeated using methylene chloride as the extraction solvent with tropylium perchlorate and potassium dichloroacetate. The only methylene chloride soluble product isolated was tropone in 18% yield.

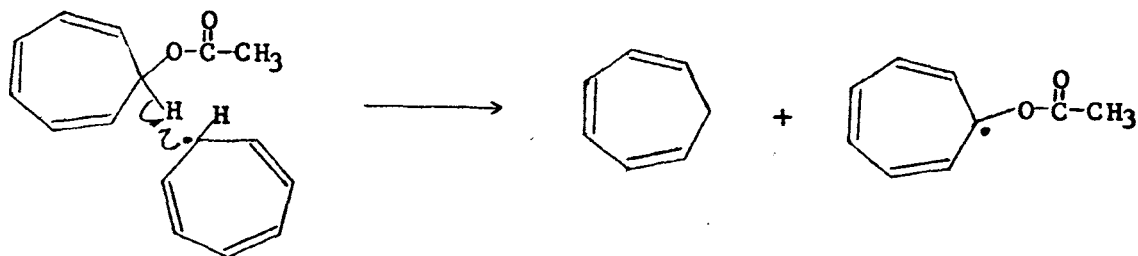
The above reaction was repeated with tropylium perchlorate and potassium trichloroacetate. When the methylene chloride was removed

from the methylene chloride extract nothing remained.

The potassium acetate salts were used because potassium perchlorate is only sparingly soluble in water. It was observed that when the tropylium perchlorate was added to an aqueous solution of the acetate salt, the tropylium ion became yellow colored, then dissolved while another white solid precipitated shortly thereafter. This second white solid was presumably potassium perchlorate. It is obvious that troyl acetate is formed since it is isolated. The only other likely primary product of these reactions is ditroyl ether. The formation of the ether requires the presence of water. The fact that tropone is formed from tropylium perchlorate and potassium chloroacetate in acetonitrile suggest that ditroyl ether is not involved in this reaction. All the above facts suggest that the troyl acetates are formed and decompose to yield tropone. Our proposed mechanism makes use of the troyl radical which has been shown to be the most stable free radical known.¹⁰³ Our proposed mechanism is shown in Chart 4 below. We did not observe any evolution of gases.

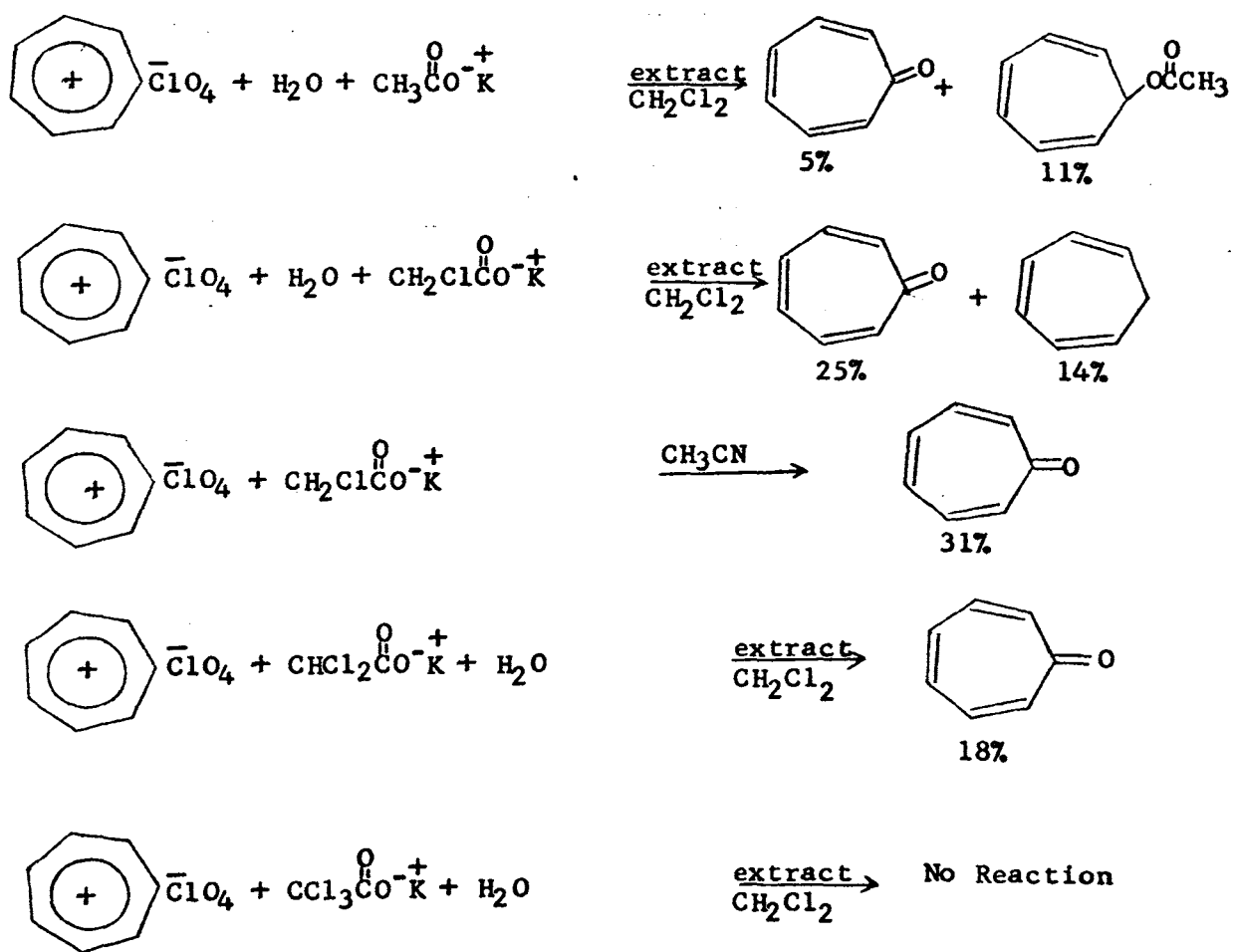
Chart 4





The tropyli acetate formed was shown by NMR, and UV spectral characteristics to be completely covalent in acetonitrile and acetone solvents.

A flow sheet of the reactions observed is shown here.



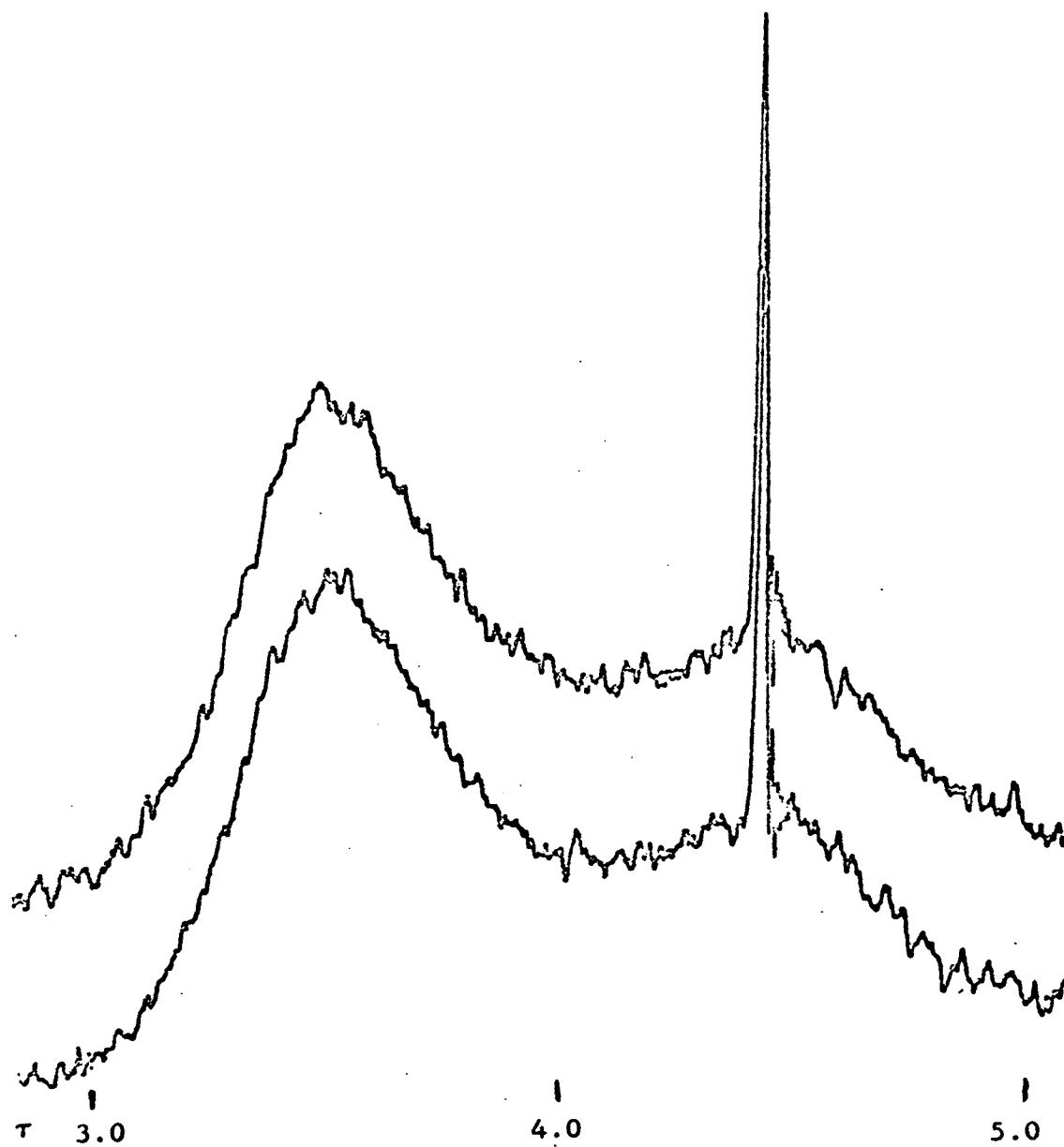


Figure 1. Tropyl Azide in Acetone - 10% Deuterium Oxide at 50° (Bottom Spectra) and at 20° (Top Spectra).

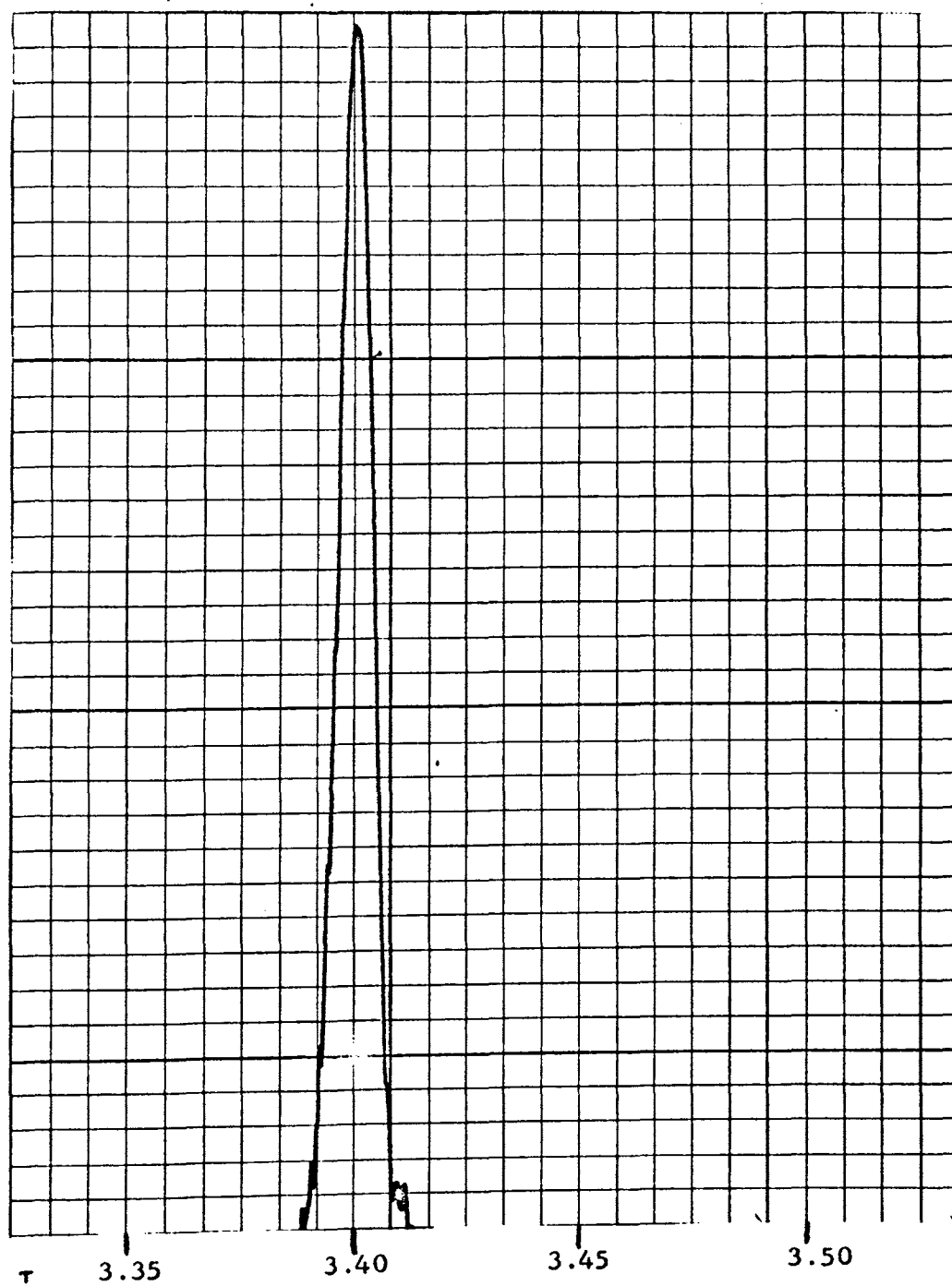


Figure 2. Tropylium Perchlorate in d_5 -Pyridine at 34° .

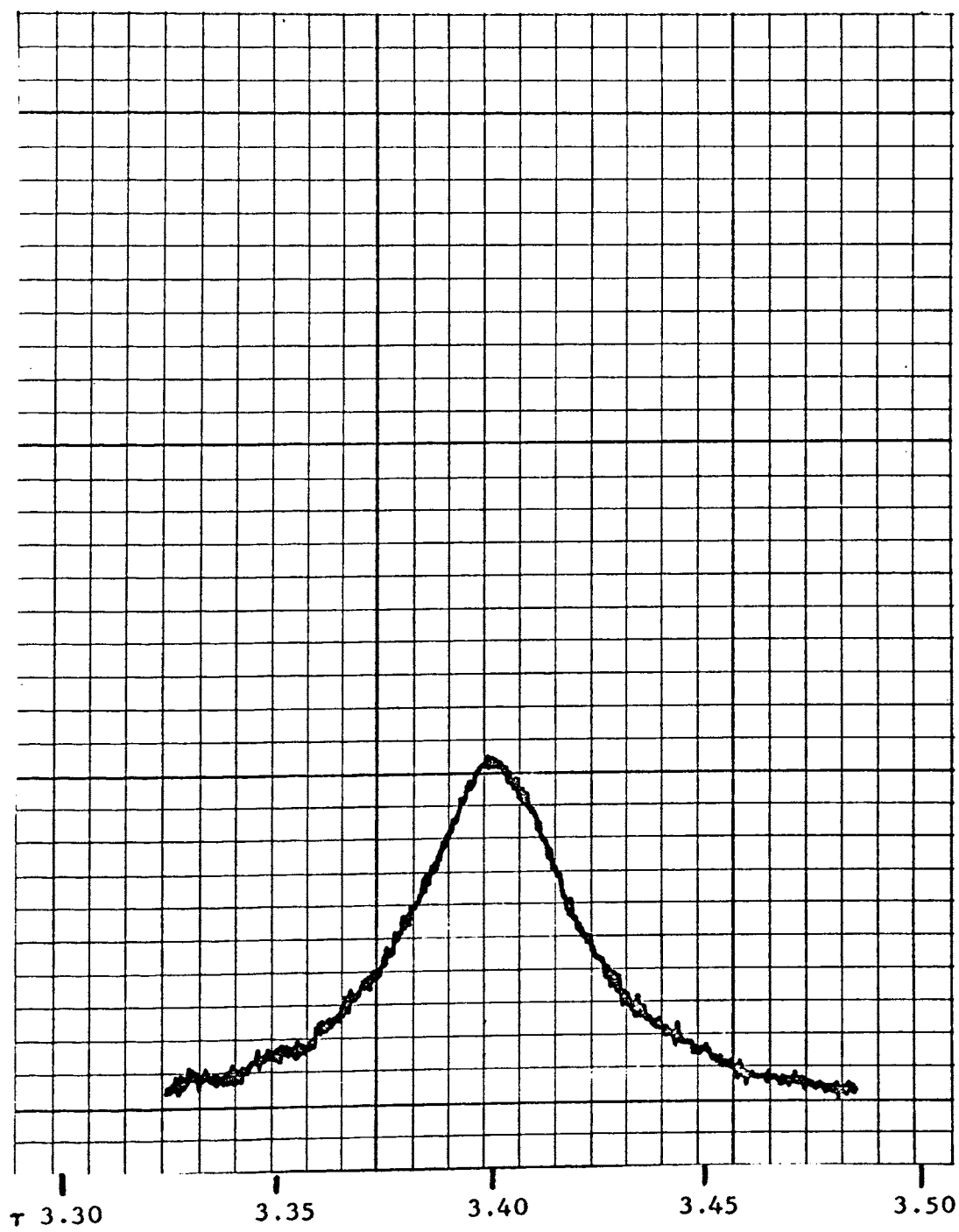


Figure 3. Tropylium Perchlorate in d_5 -Pyridine at 0° .

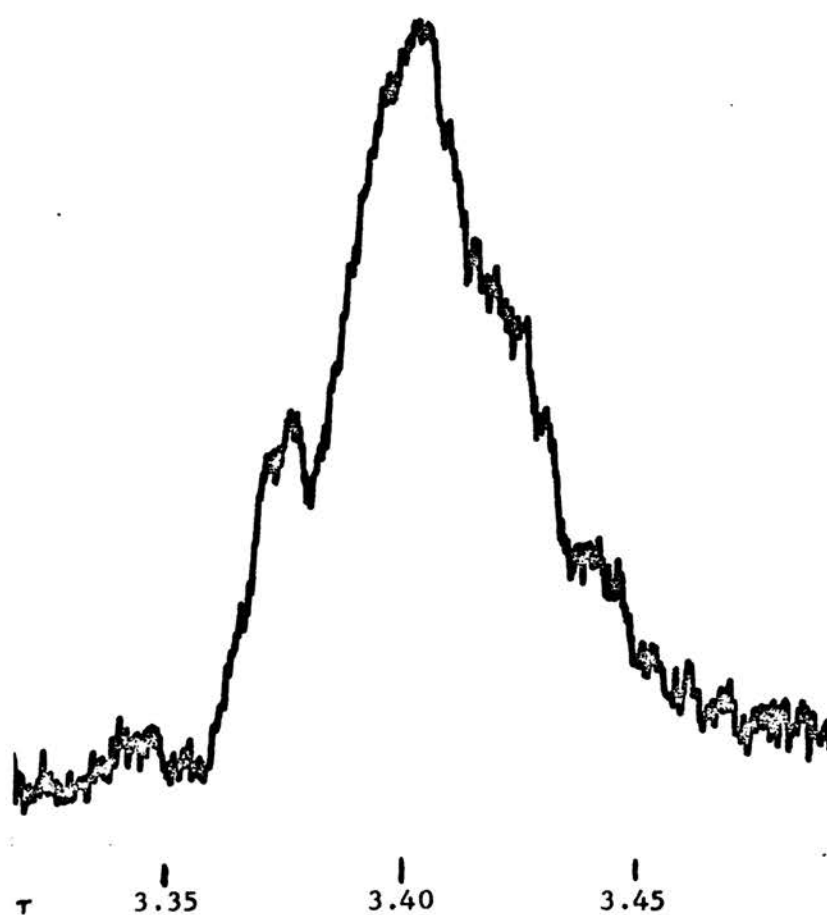


Figure 4. Tropylium Perchlorate in d_5 -Pyridine at -20° .

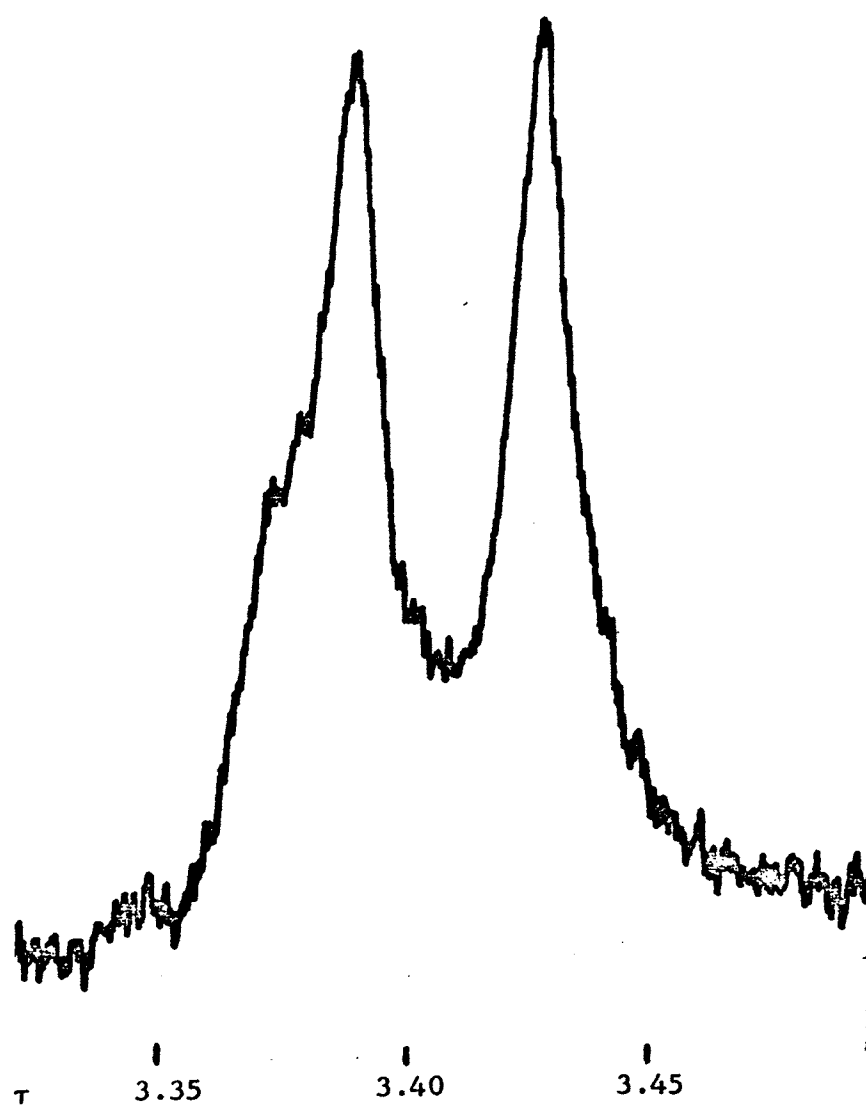


Figure 5. Tropylium Perchlorate in d_5 -Pyridine at -40° .

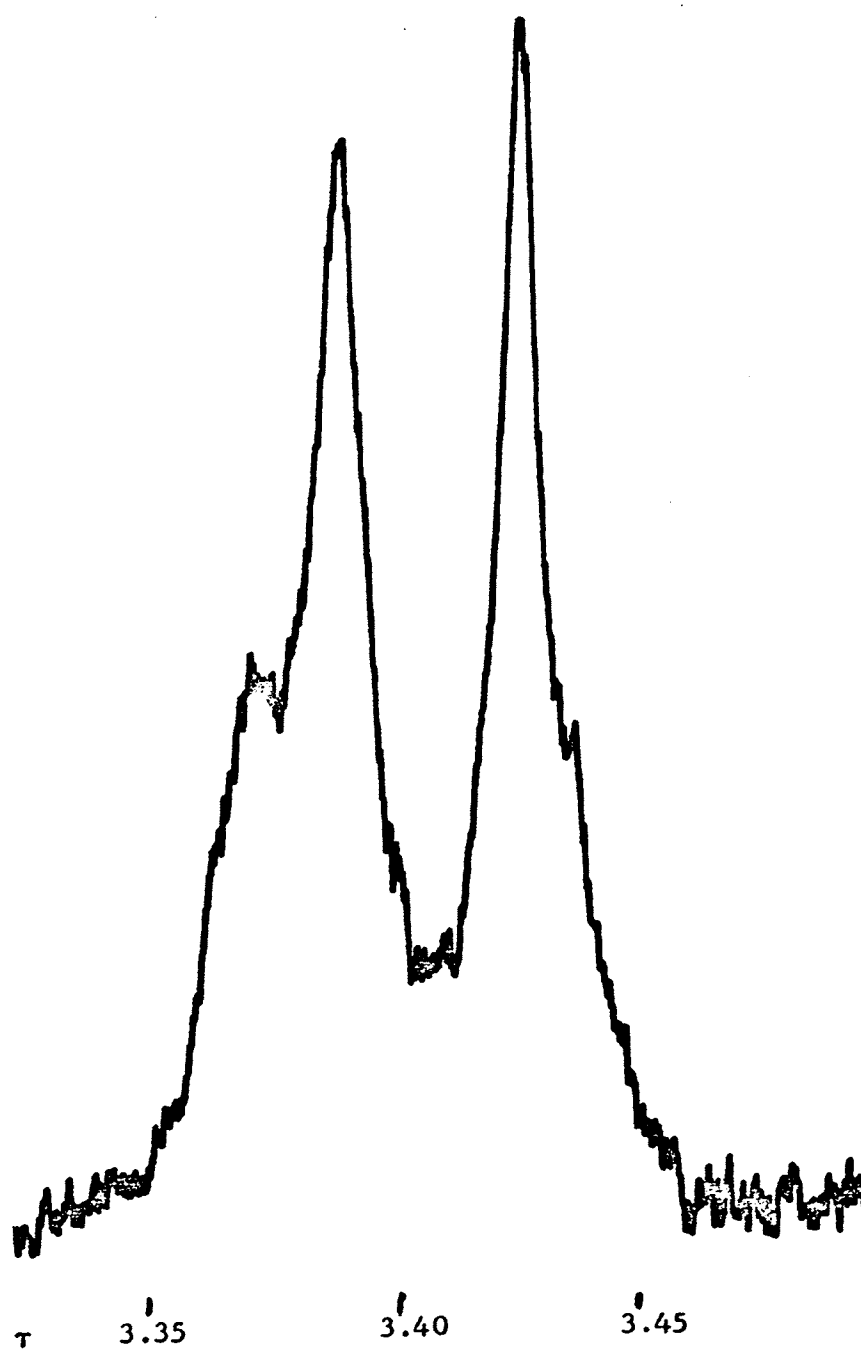


Figure 6. Tropylium Perchlorate in d_5 -Pyridine at -70° .

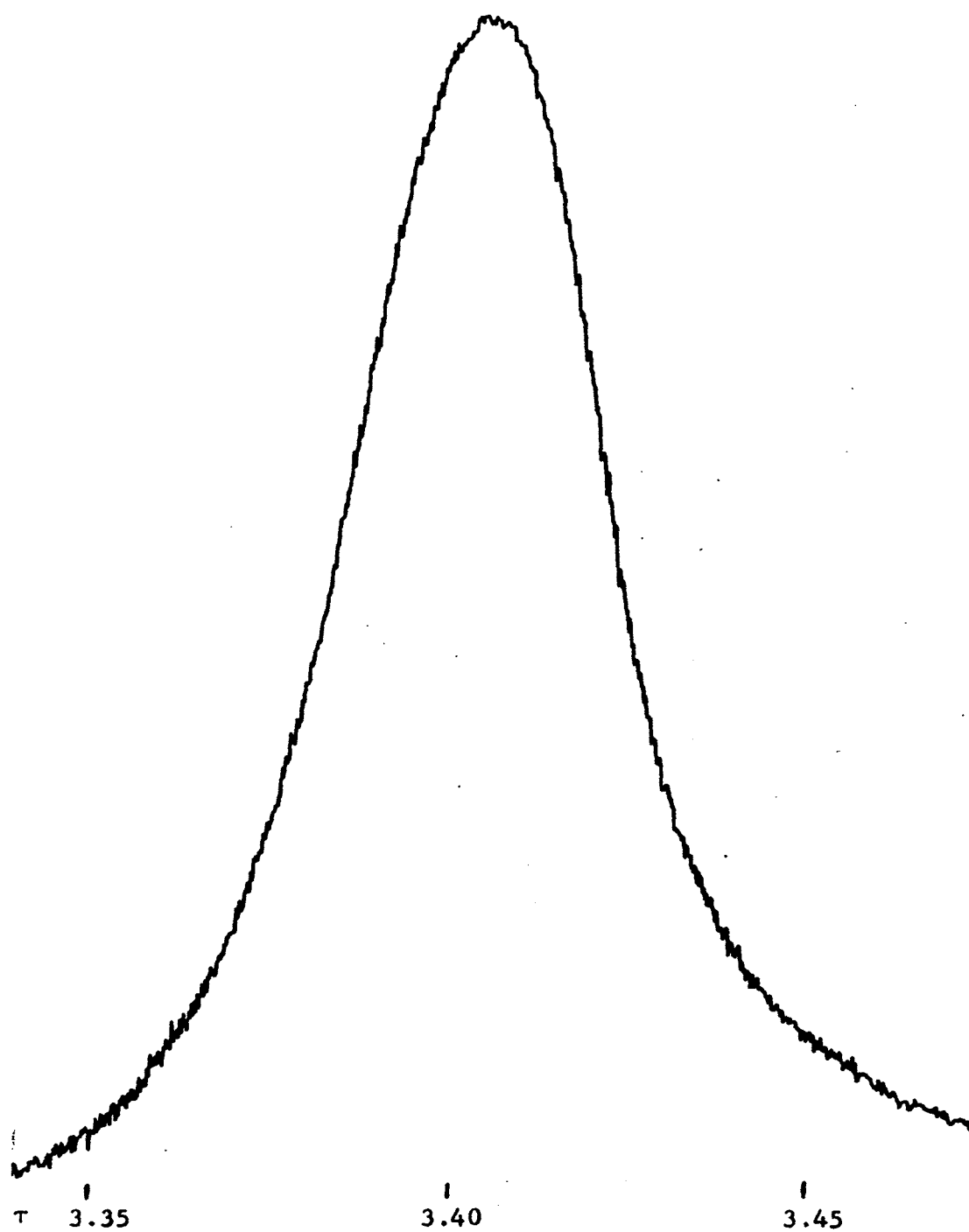


Figure 7. Tropylium Perchlorate and d_5 -Pyridine in Acetone at 34° .

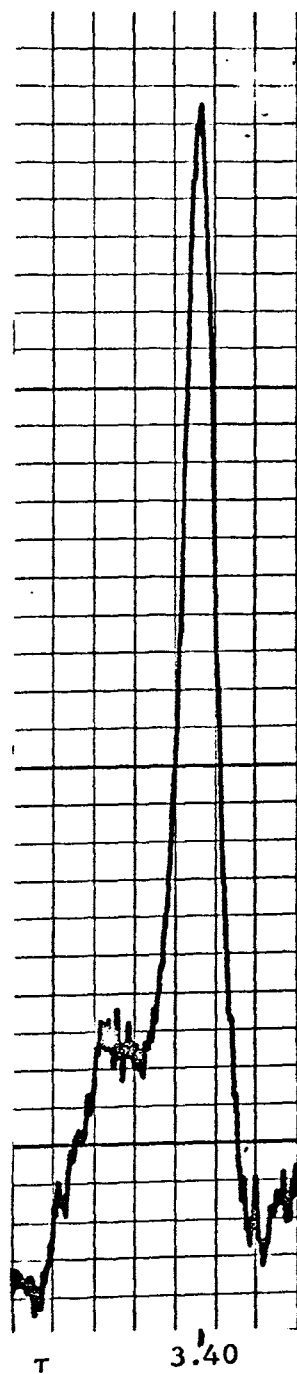


Figure 8. Tropylium Perchlorate and d_5 -Pyridine in Acetone at 10° .

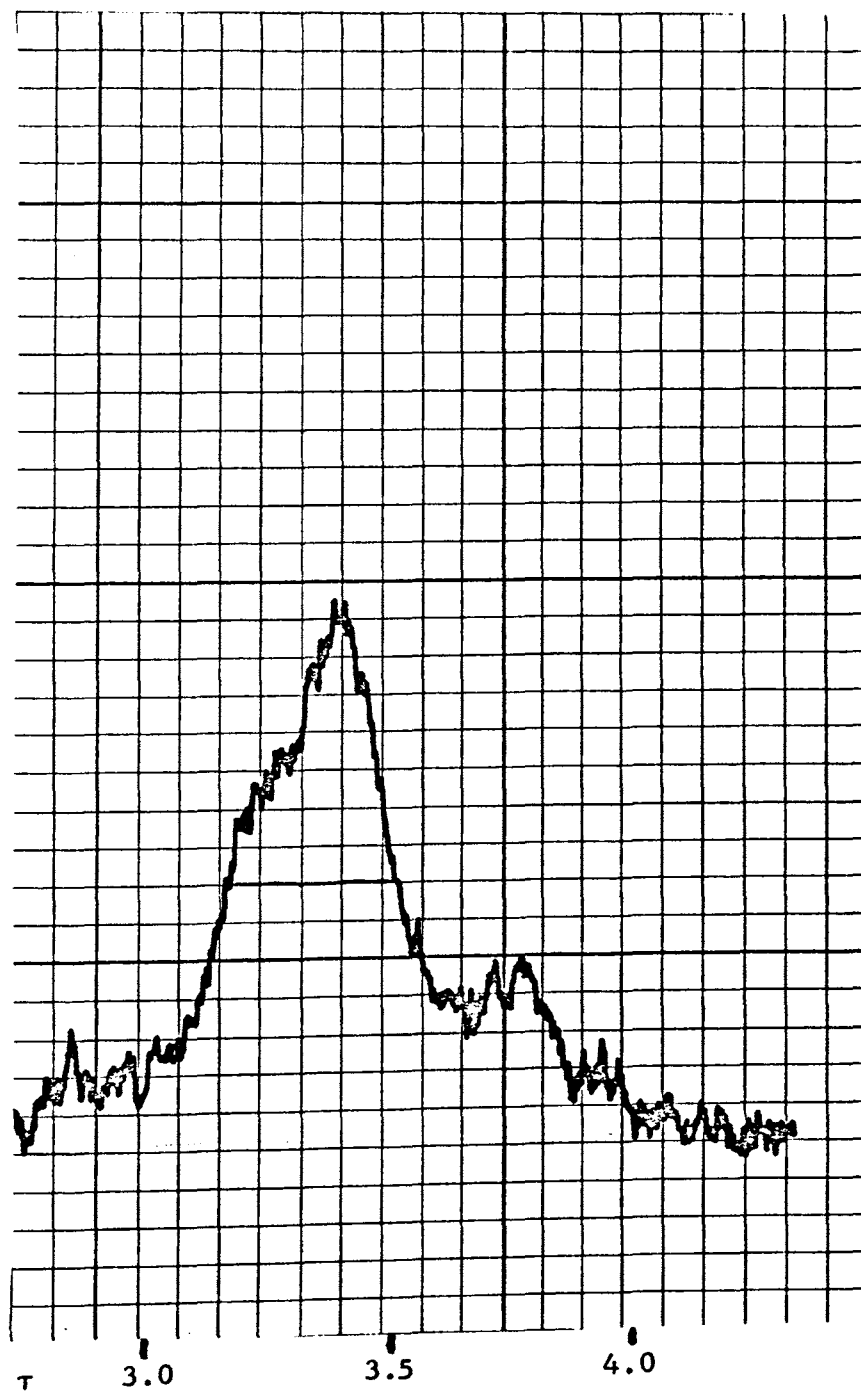


Figure 9. Tropylium Perchlorate and d_5 -Pyridine in Acetone at -10° .

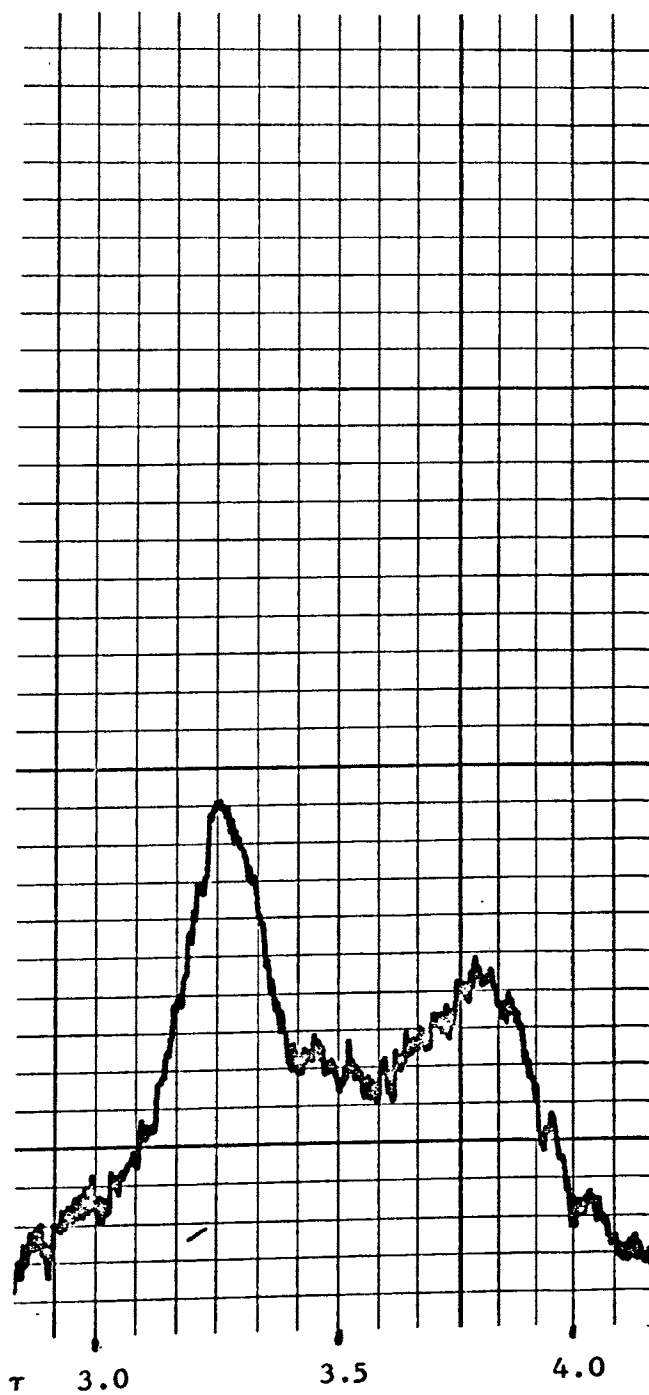


Figure 10. Tropylium Perchlorate and d_5 -Pyridine in Acetone -30° .

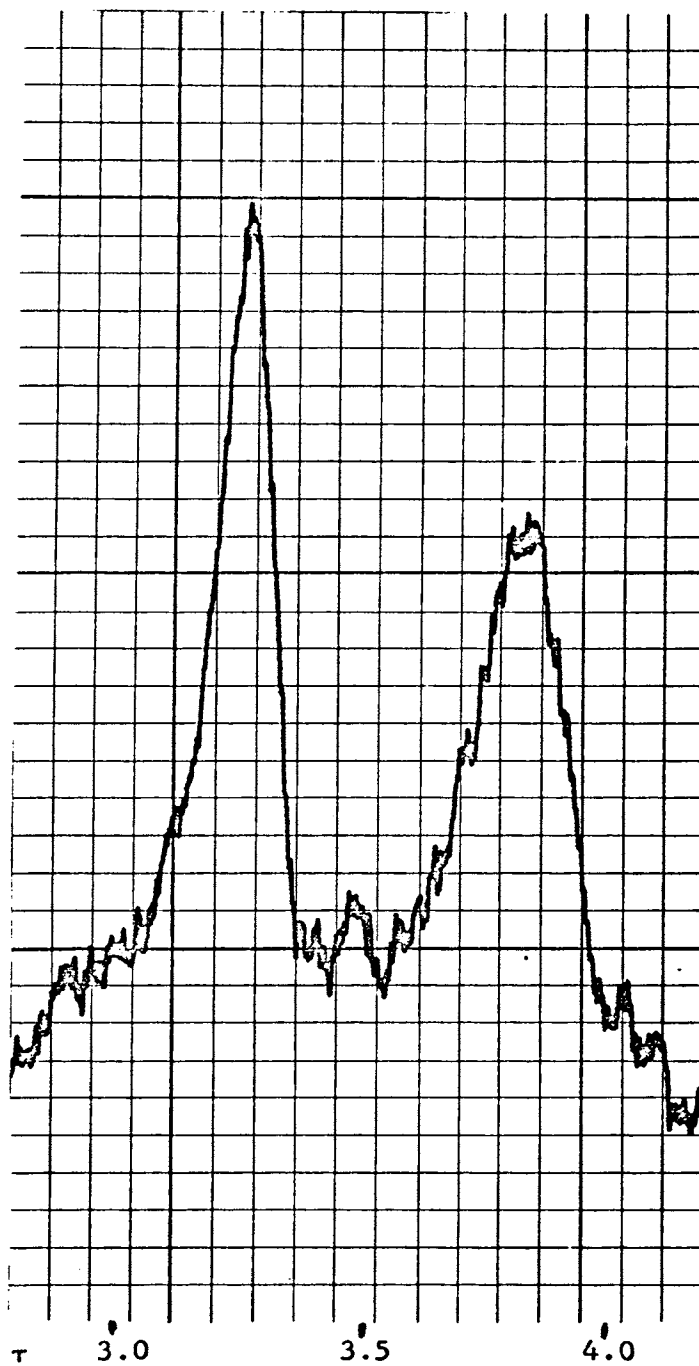


Figure 1L Tropylium Perchlorate and d_5 -Pyridine in Acetone at -70° .

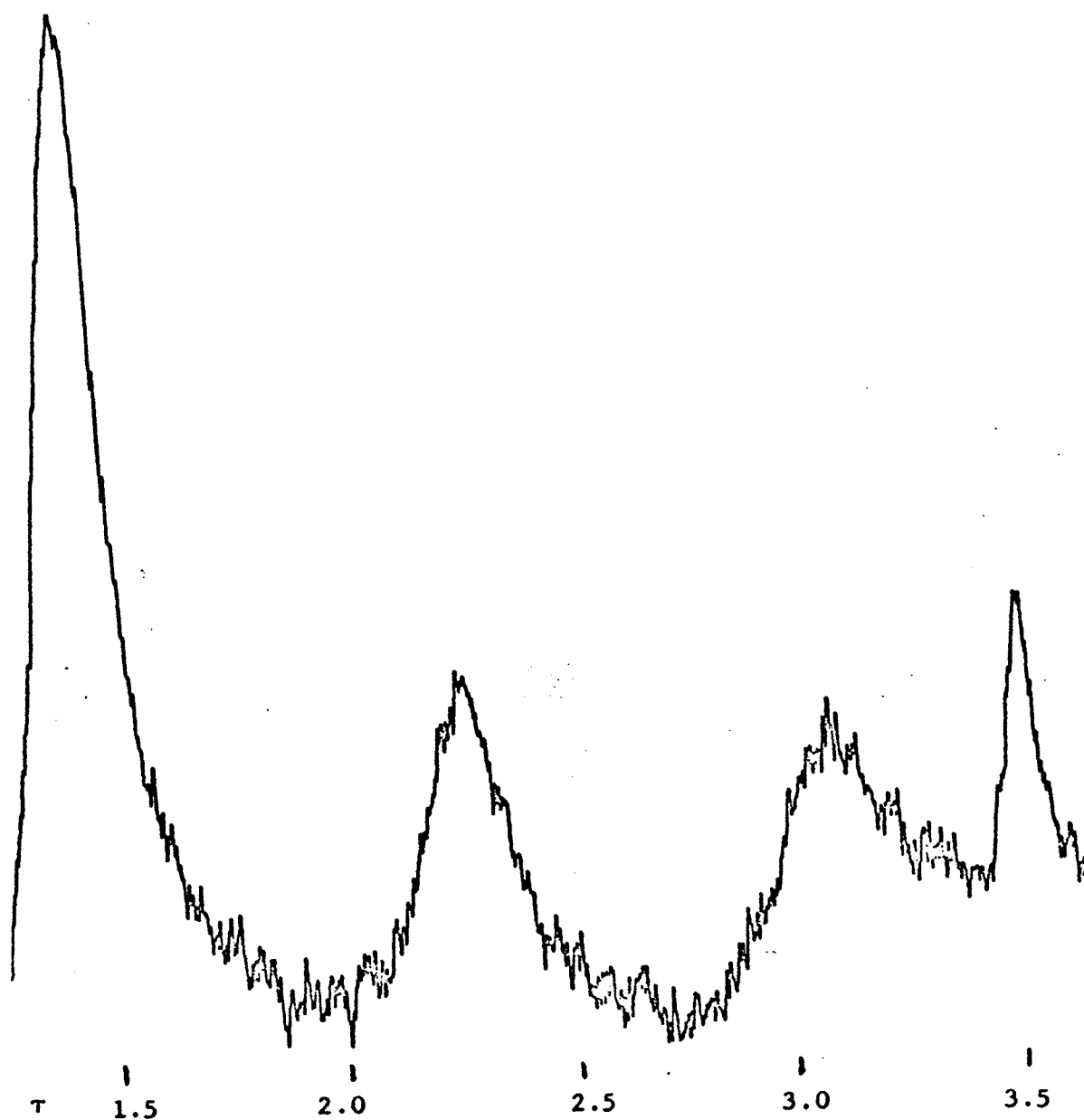


Figure 12. 3,5 Lutidine and Tropylium Perchlorate in d_6 -Acetone at 35° .

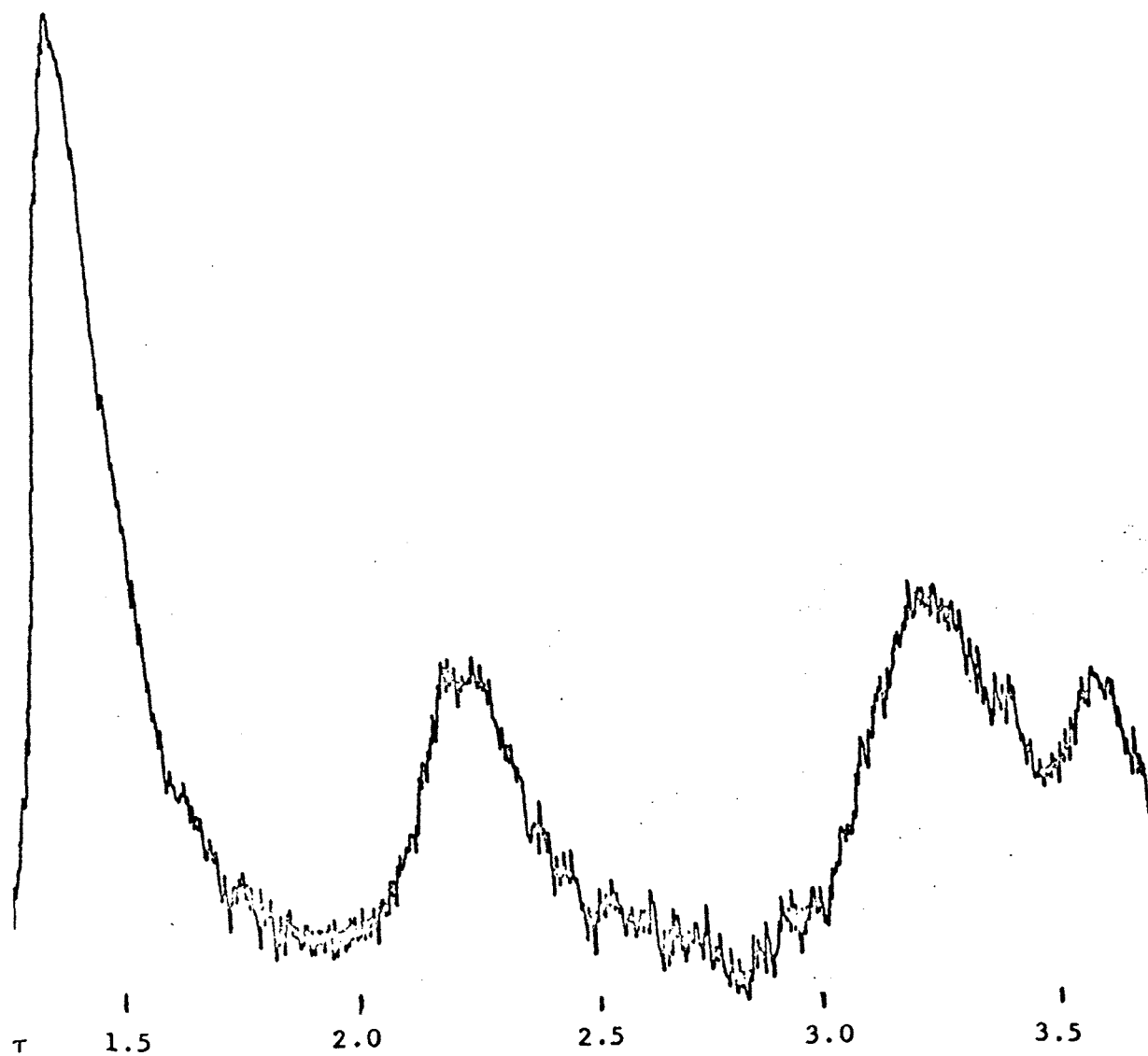


Figure 13. 3,5 Lutidine and Tropylium Perchlorate in d_6 -Acetone at 20°.

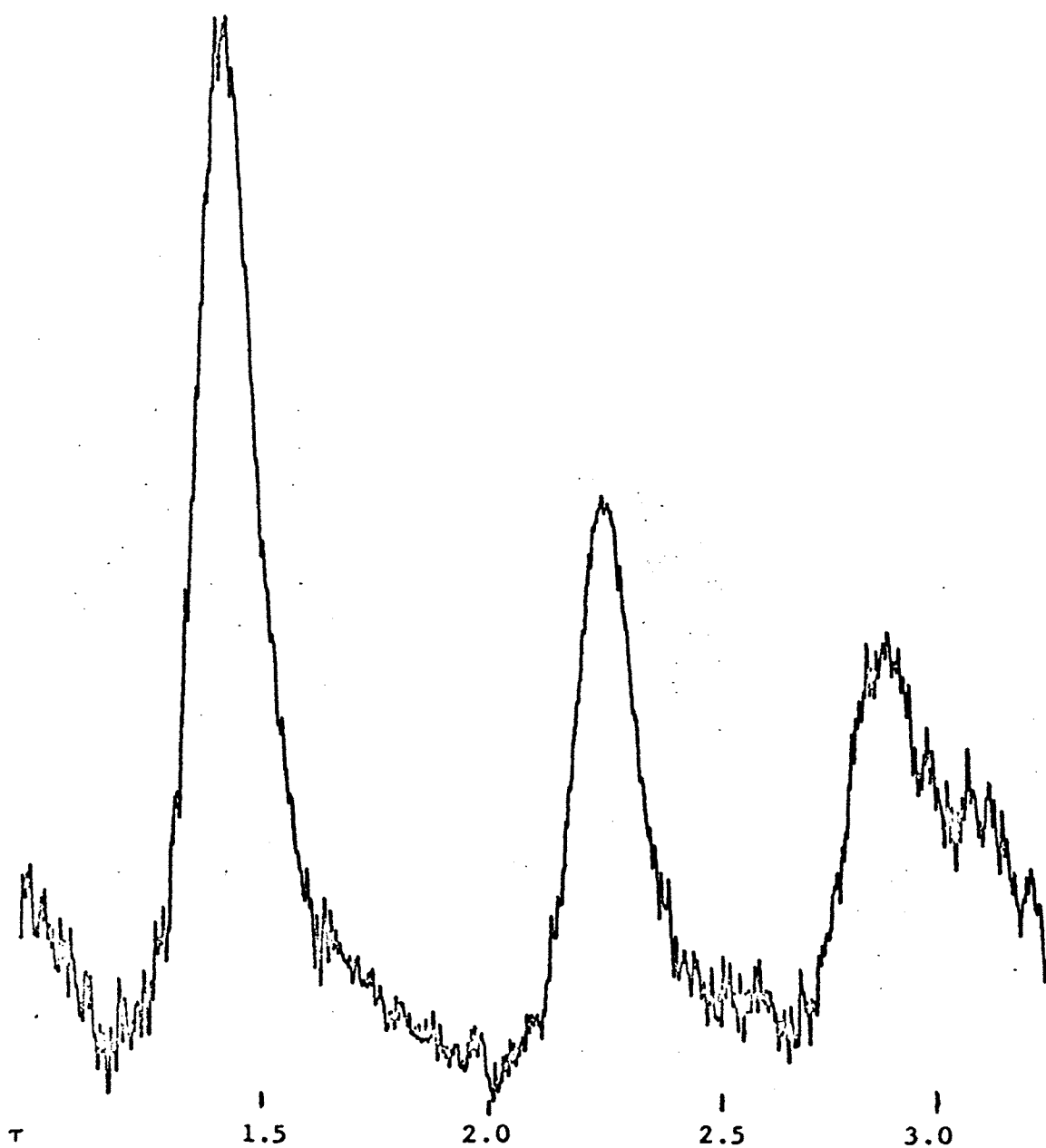


Figure 14. 3,5 Lutidine and Tropylium Perchlorate in d_6 -Acetone at 0° .

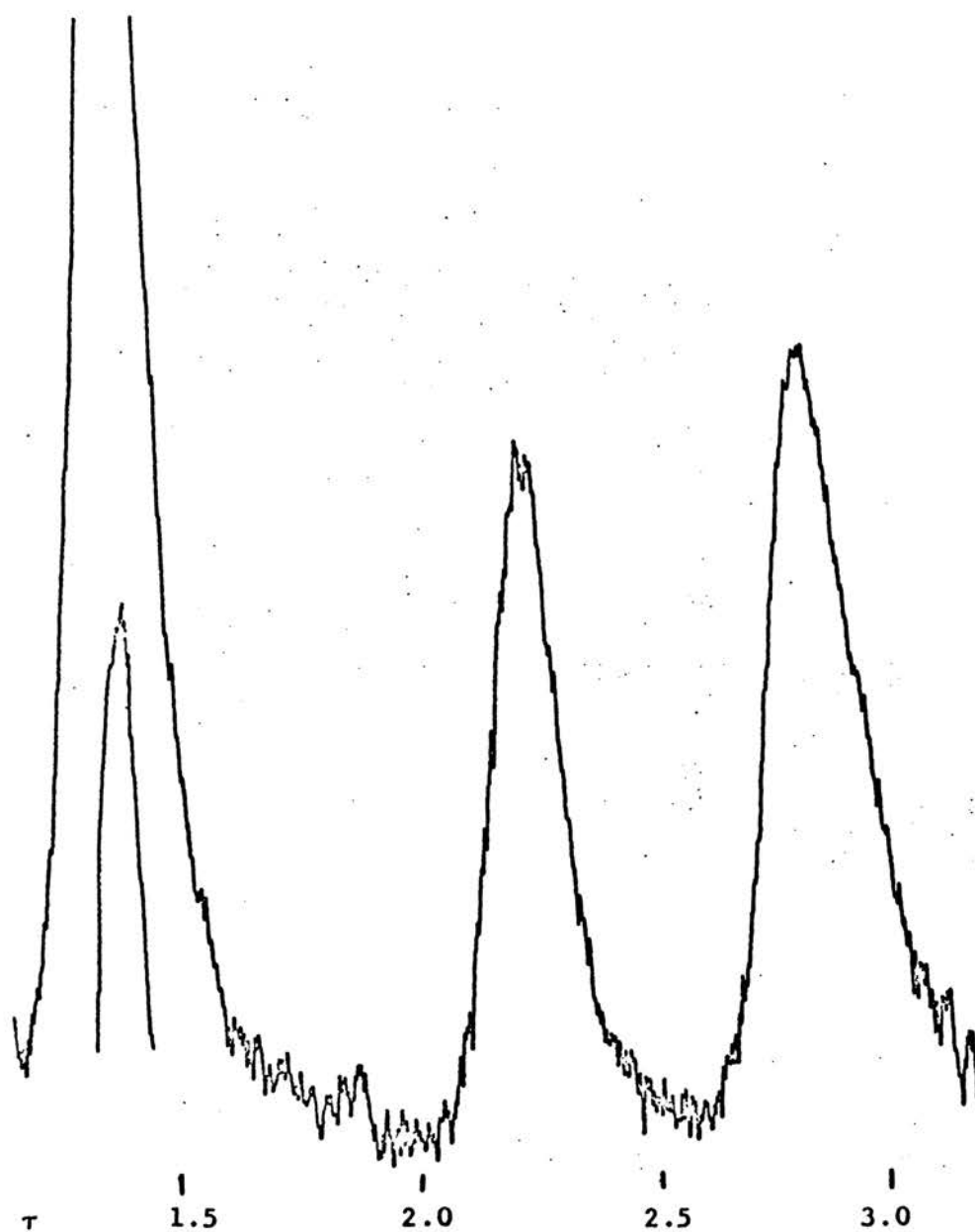


Figure 15a. 3,5 Lutidine and Tropylium Perchlorate in d_6 -Acetone at -20° .

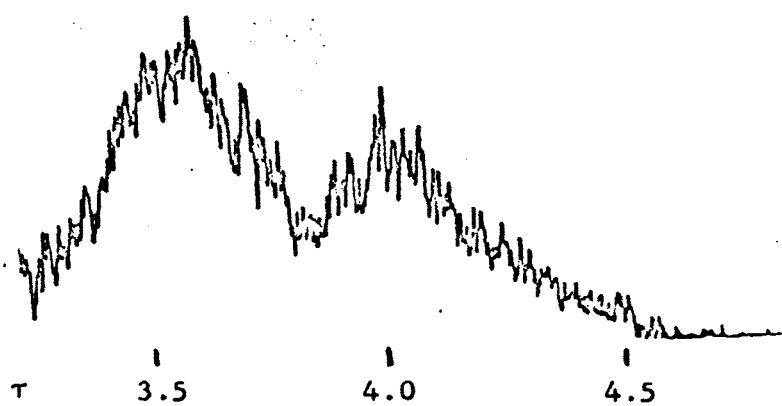


Figure 15b. 3,5 Lutidine and Tropylium Perchlorate in d_6 -Acetone at -20° .

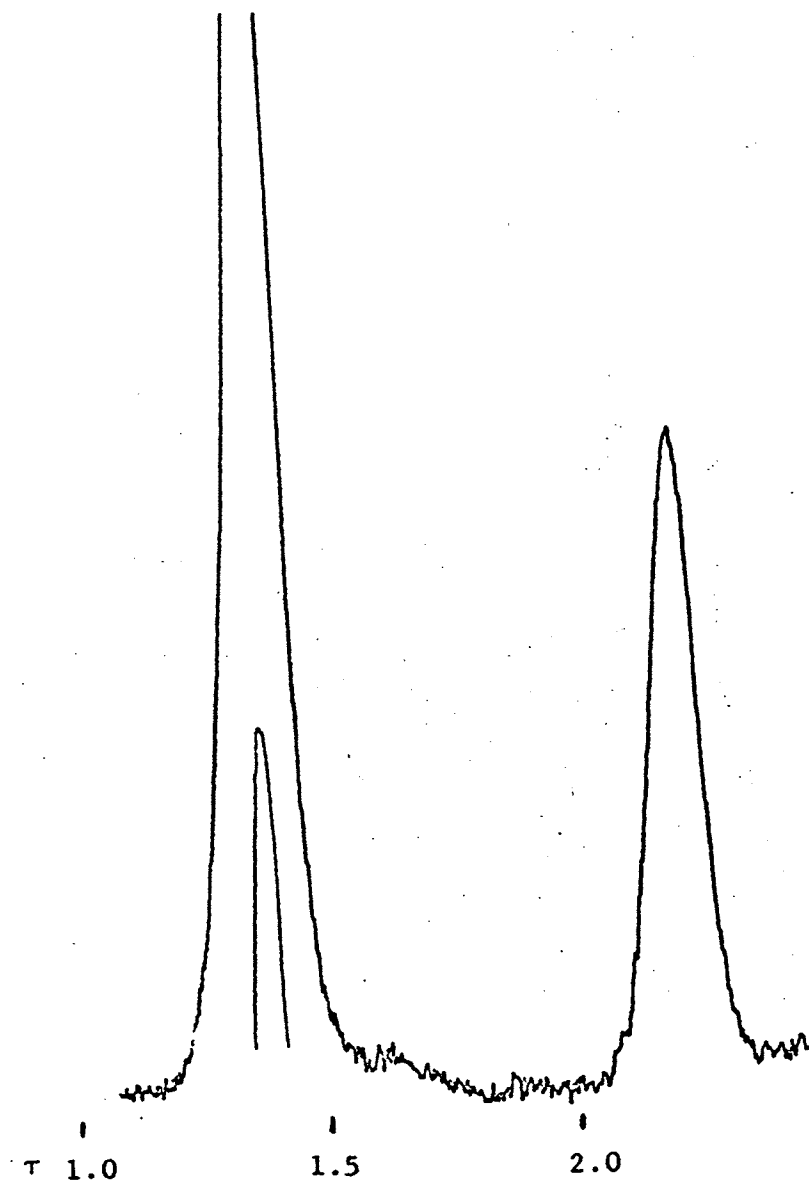


Figure 16a. 3,5 Lutidine and Tropylium Perchlorate in d_6 -Acetone at -40° .

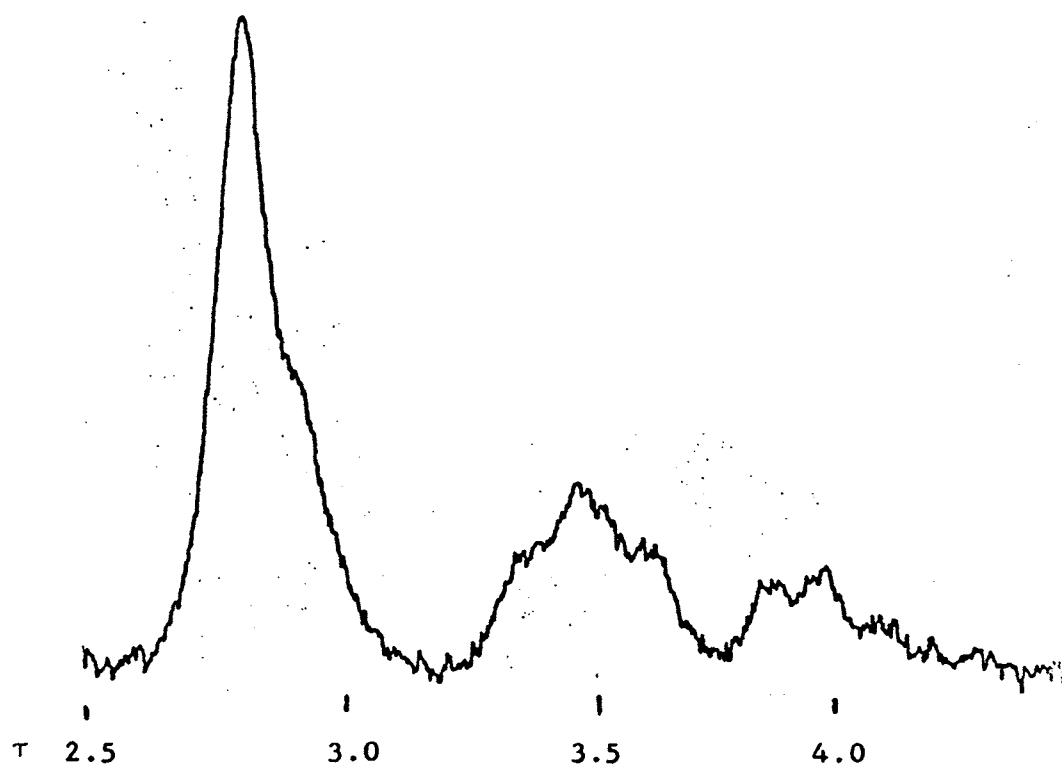


Figure 16b. 3,5 Lutidine and Tropylium Perchlorate in d_6 -Acetone at -40° .

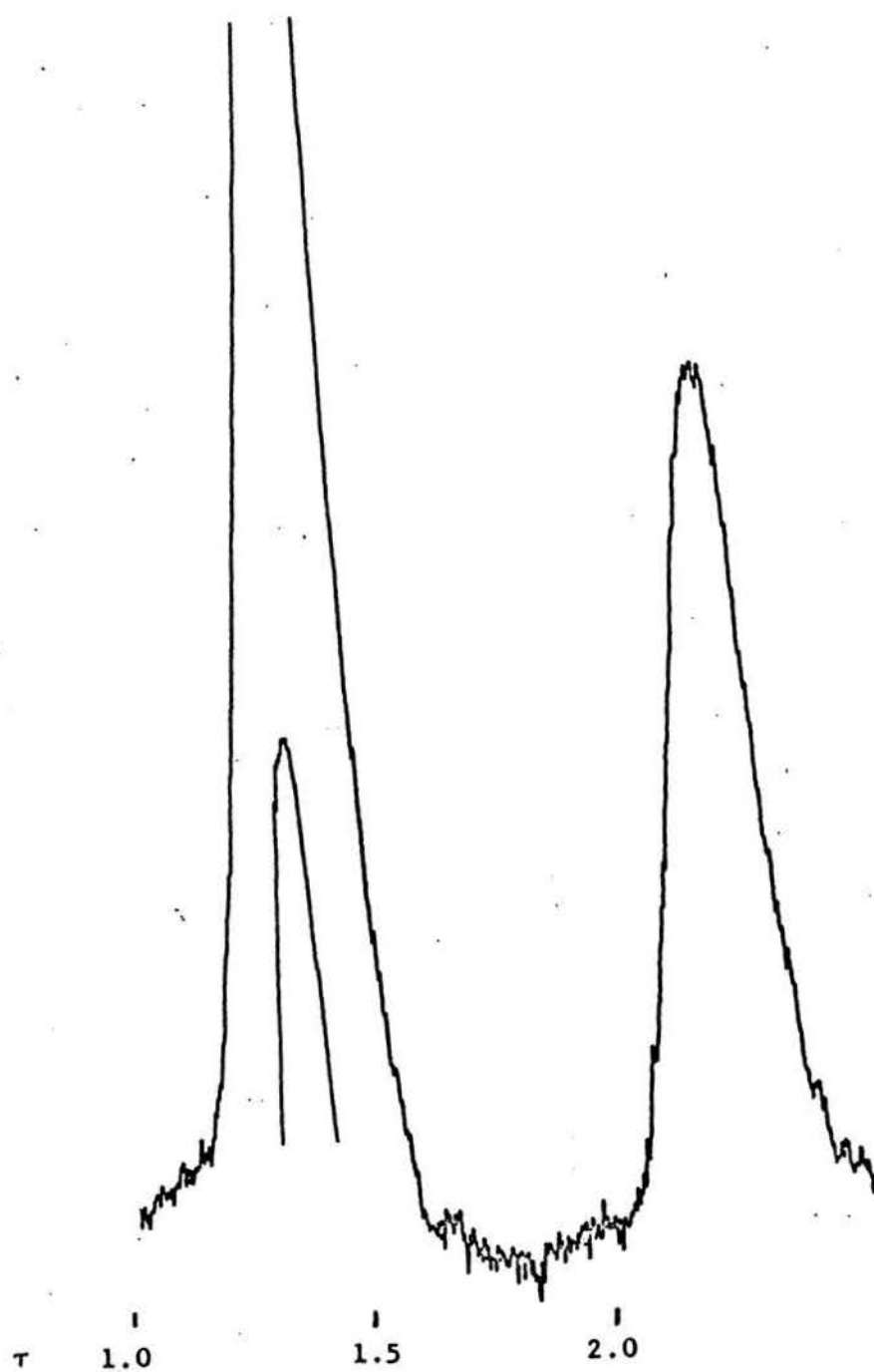


Figure 17a. 3,5 Lutidine and Tropylium Perchlorate in d_6 -Acetone at -60° .

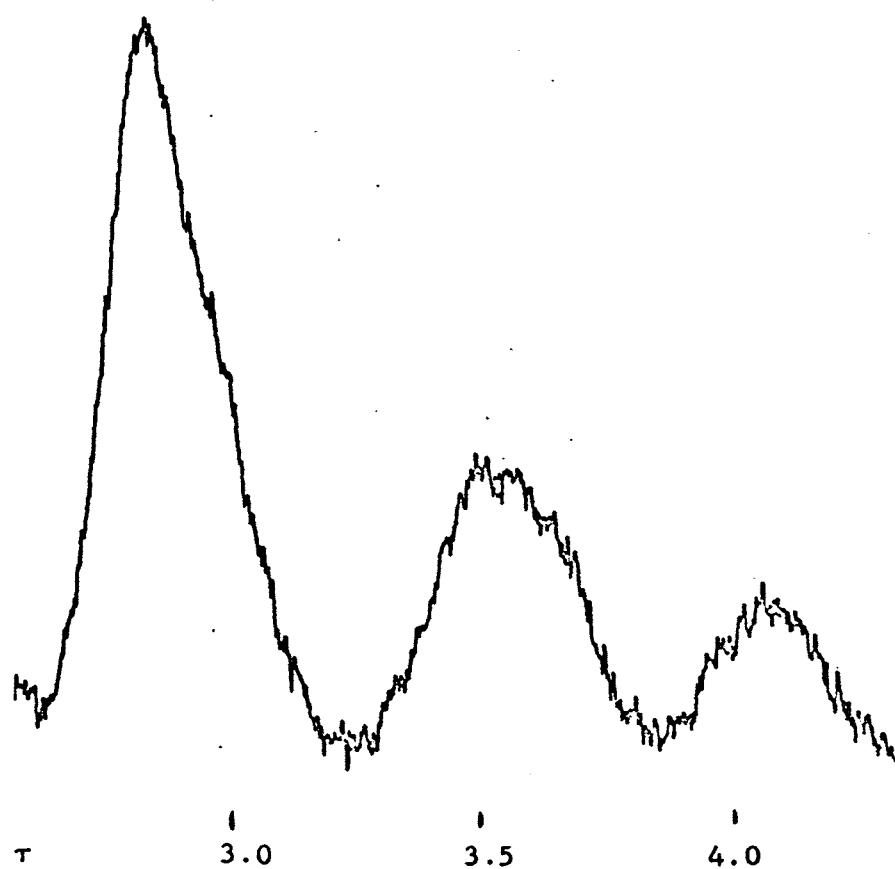


Figure 17b. 3,5 Lutidine and Tropylium Perchlorate in d_6 -Acetone at -60° .

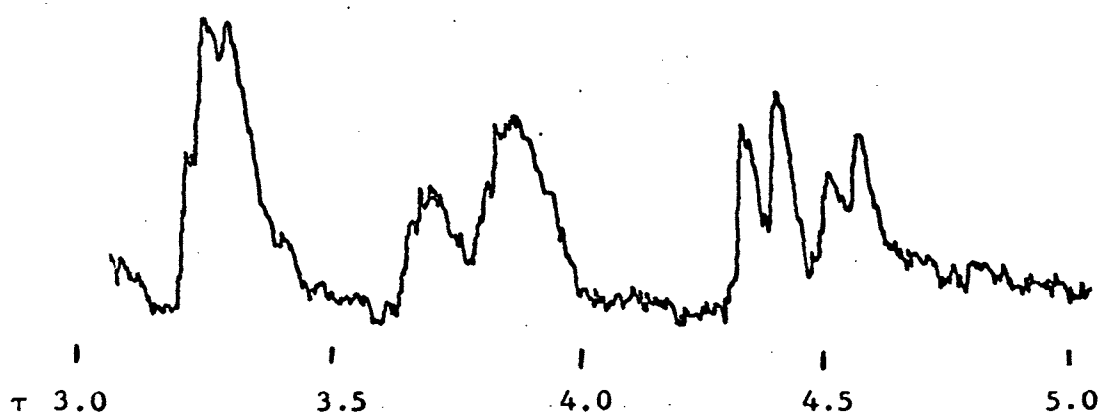


Figure 18. Tropylium Perchlorate in 2-Picoline at 34° After 1 Hour.

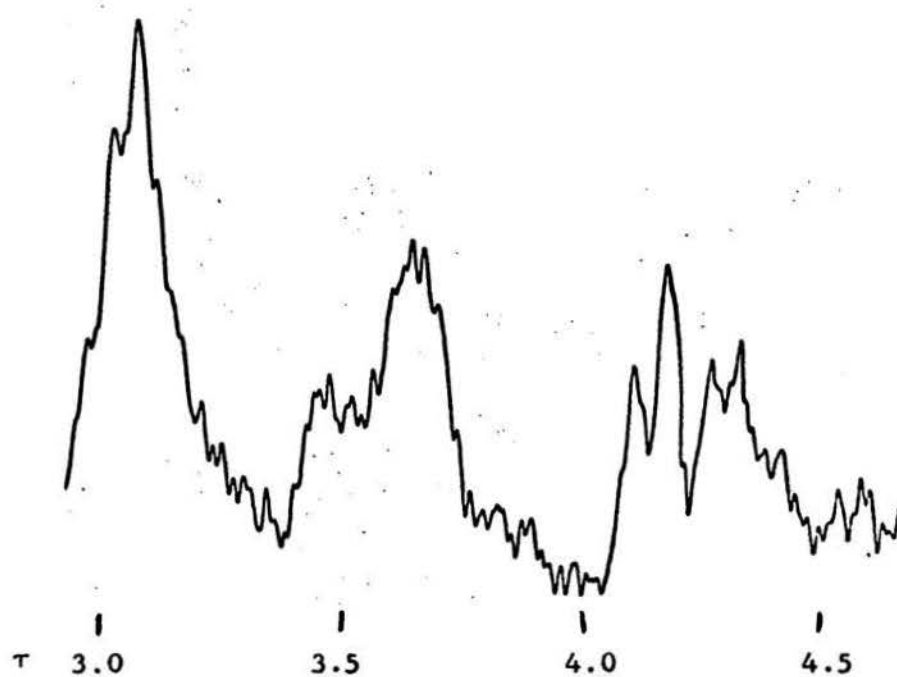


Figure 19. 2,4 Lutidine and Tropylium Perchlorate in d_6 -Acetone at 34° .

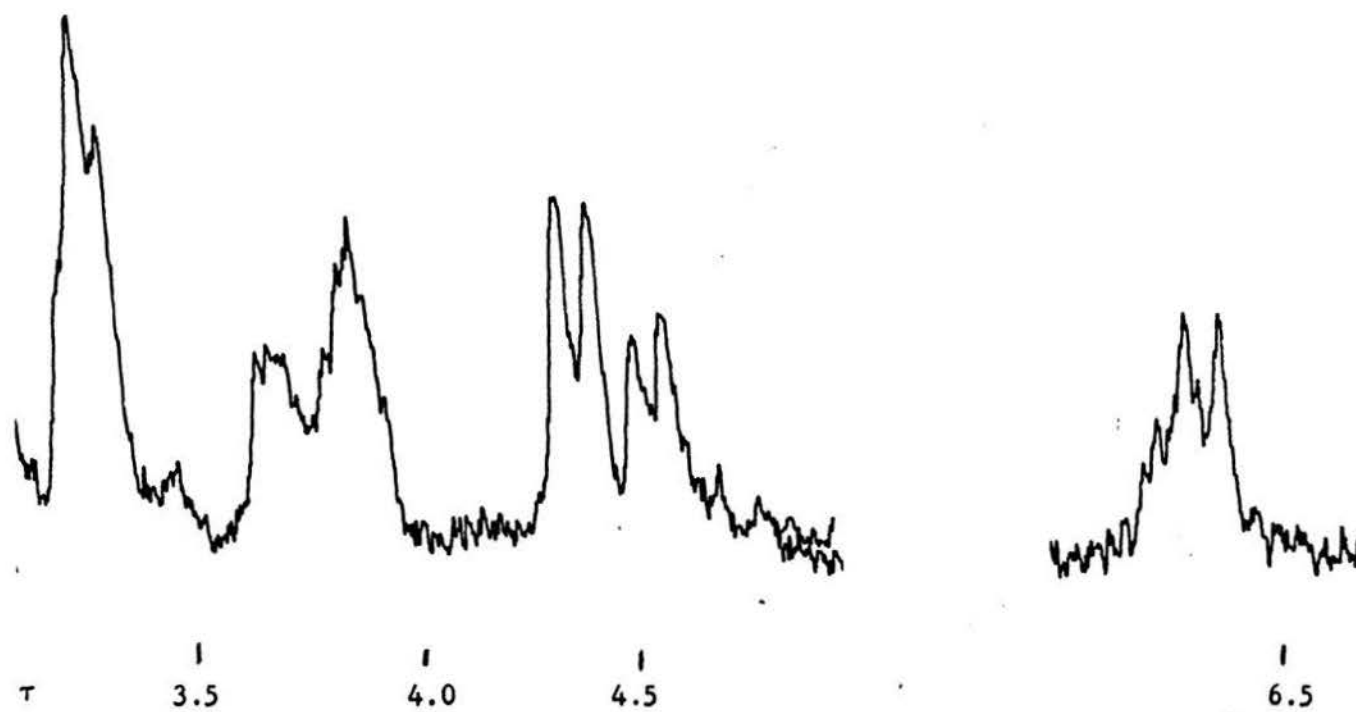


Figure 20. 2,6 Lutidine and Tropylium Perchlorate in d_6 -Acetone at 34° after 1 hour.

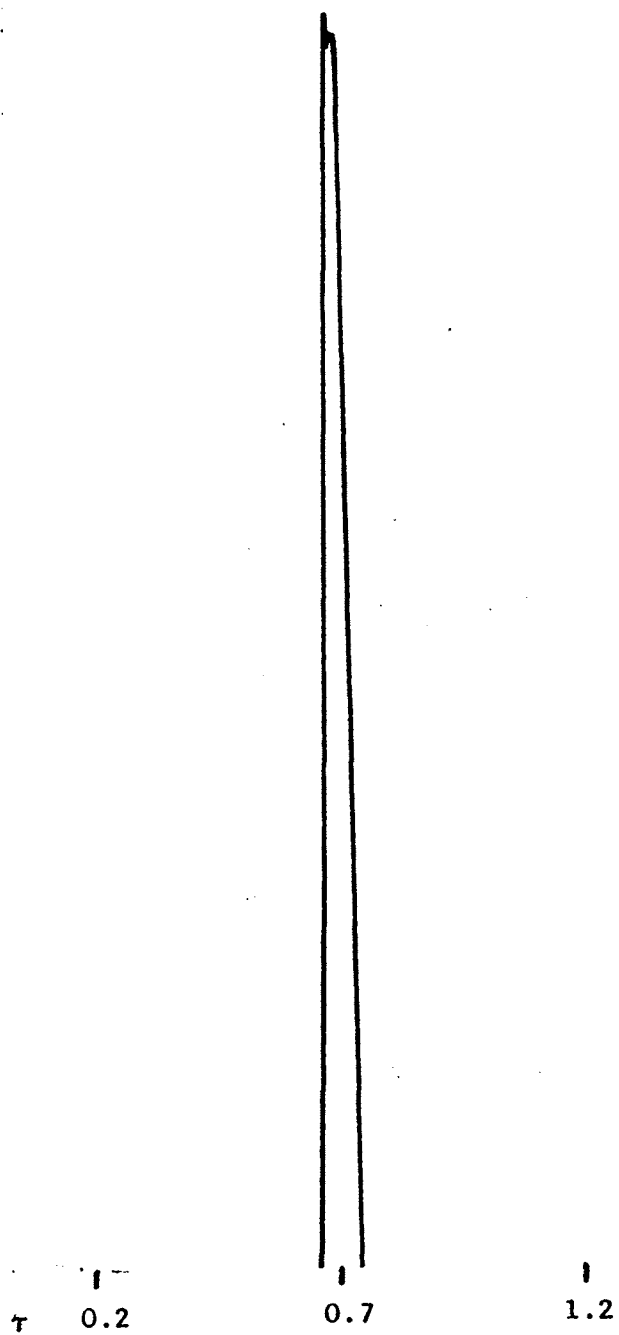


Figure 21a. Tropylium Perchlorate in Dimethylsulfoxide After 5 Minutes.

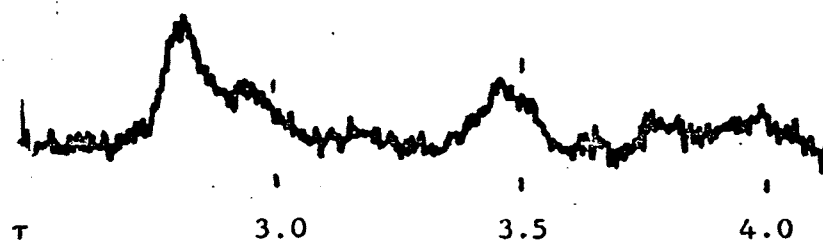


Figure 21b. Tropylium Perchlorate in Dimethylsulfoxide After 5 Minutes.

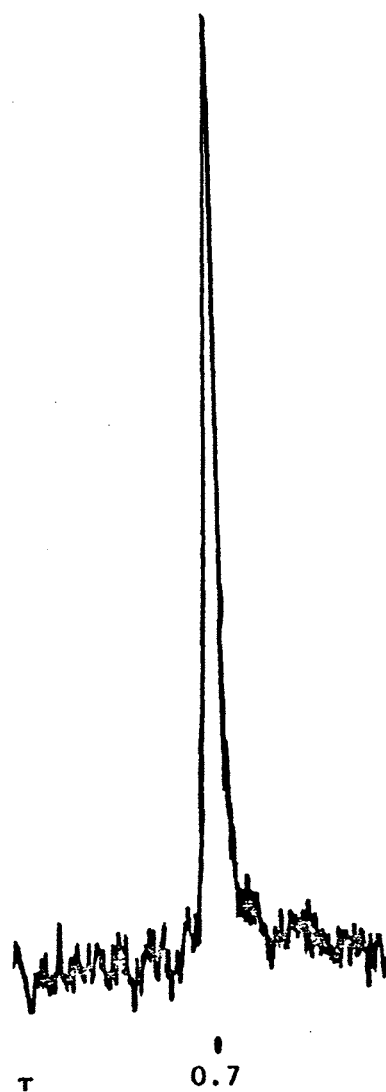


Figure 22a. Tropylium Perchlorate in Dimethylsulfoxide After 18 Hours.

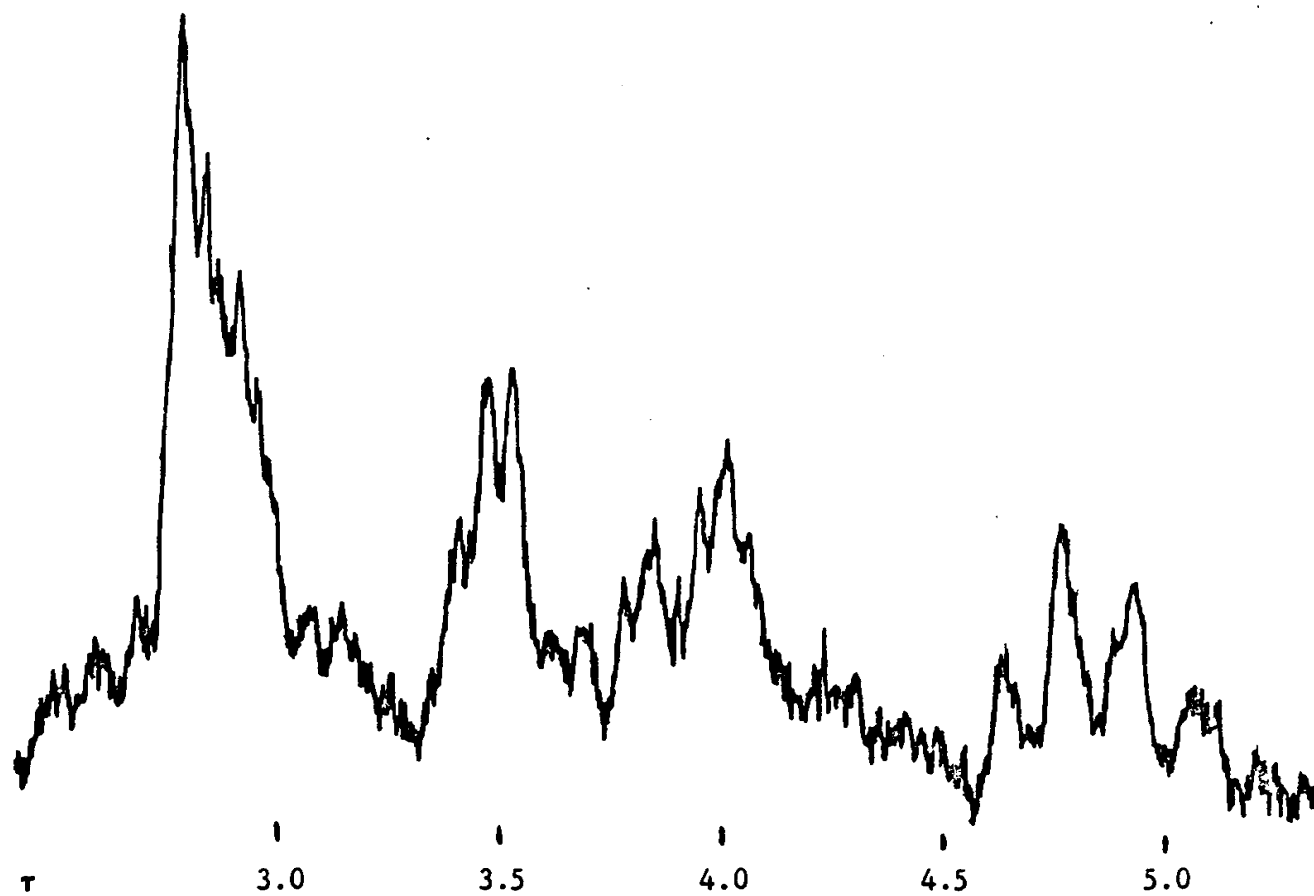


Figure 22b. Tropylium Perchlorate in Dimethylsulfoxide After 18 Hours.

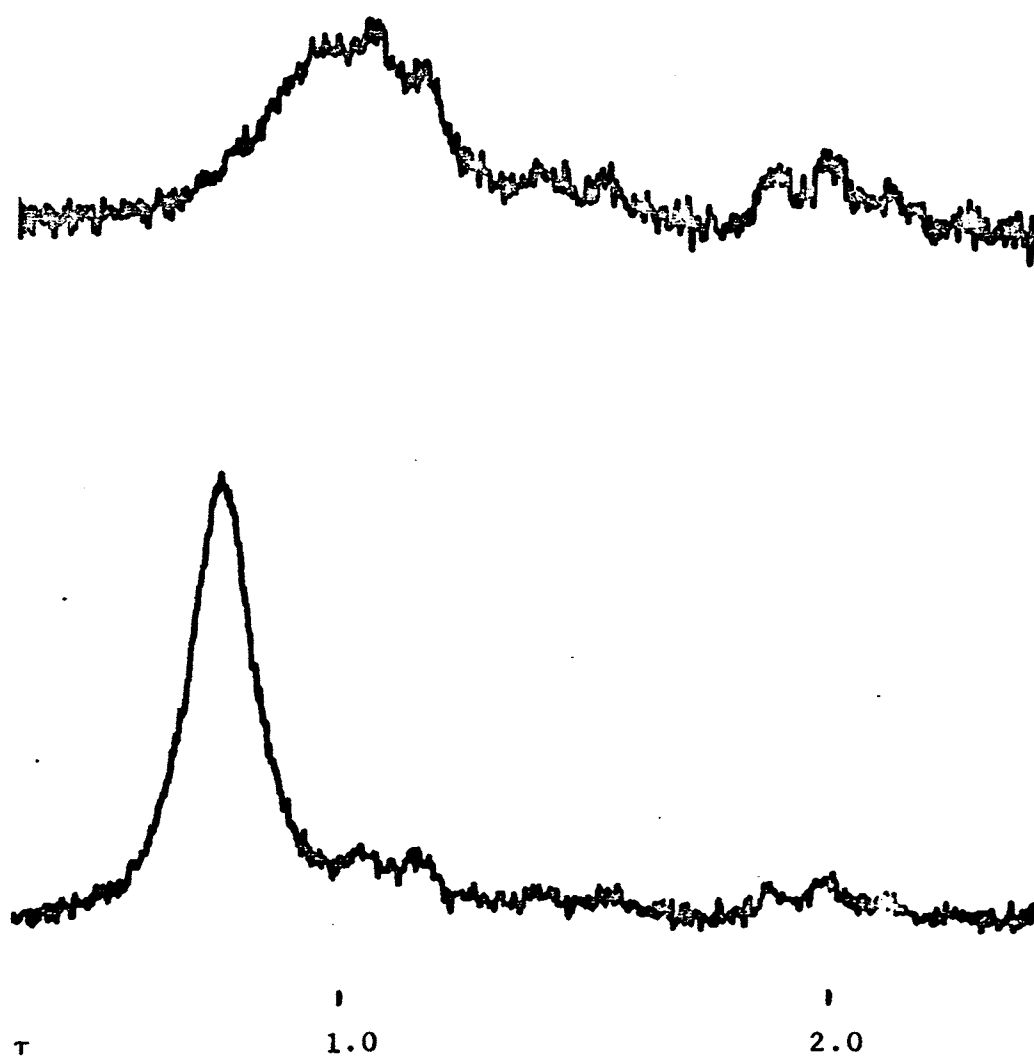


Figure 23a. Tropylium Perchlorate in Dimethylsulfoxide Plus 1 Drop of Pyridine (Bottom Spectra) and 2 Drops of Pyridine (Top Spectra).

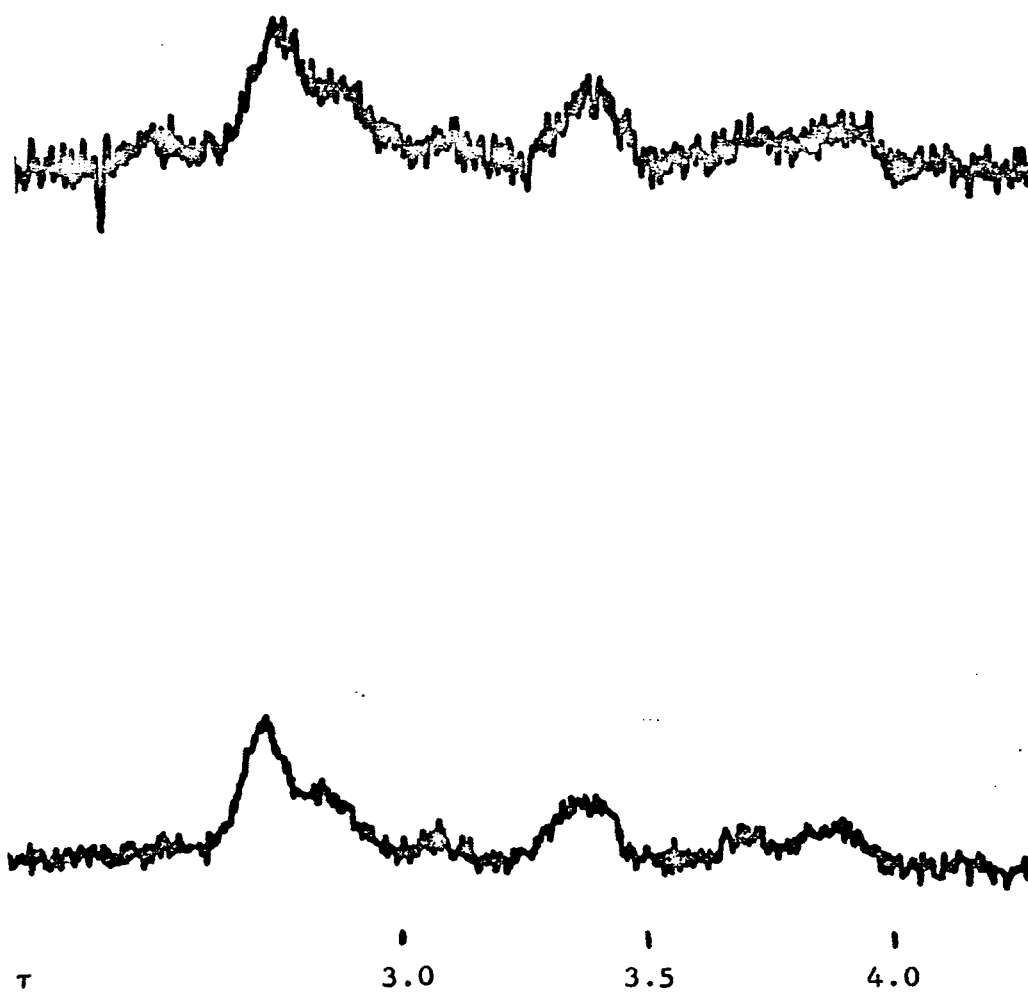


Figure 23b. Tropylium Perchlorate in Dimethylsulfoxide Plus 1 Drop of Pyridine (Bottom Spectra) and 2 Drops of Pyridine (Top Spectra).

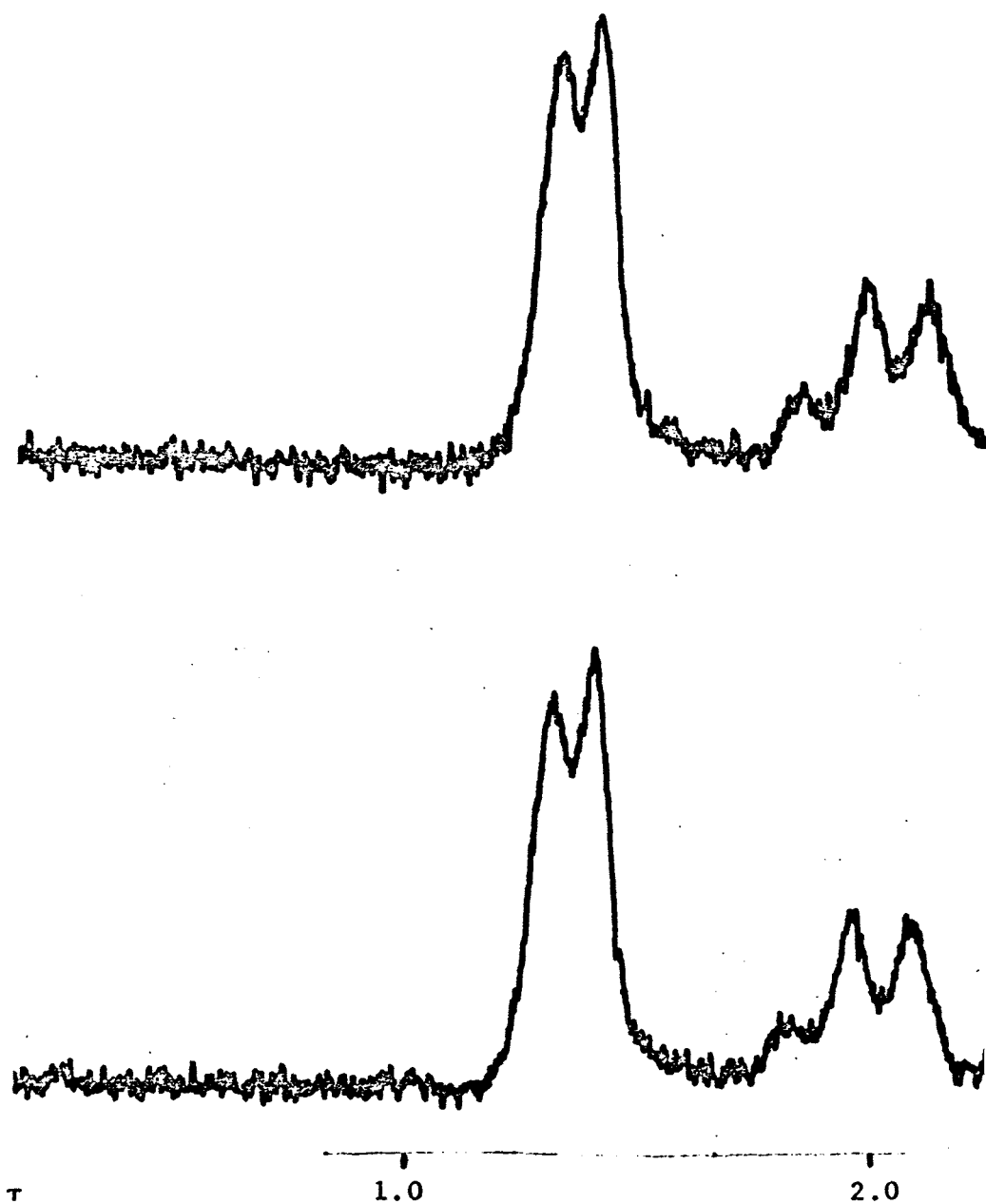


Figure 24a. Tropylium Perchlorate in Dimethylsulfoxide Plus 4 Drops of Pyridine (Bottom Spectra) and 6 Drops of Pyridine (Top Spectra).

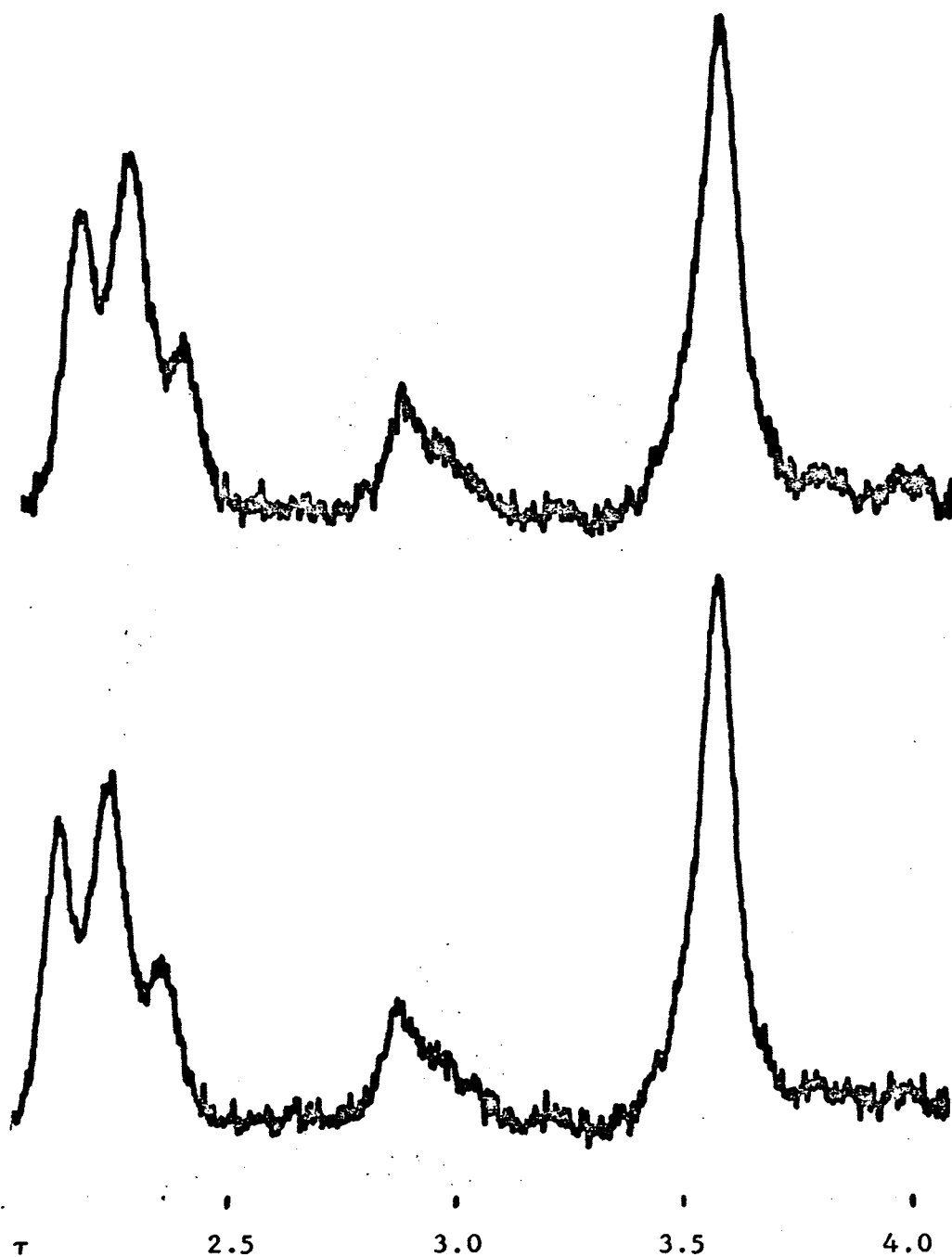


Figure 24b. Tropylium Perchlorate in Dimethylsulfoxide Plus 4 Drops of Pyridine (Bottom Spectra) and 6 Drops of Pyridine (Top Spectra).

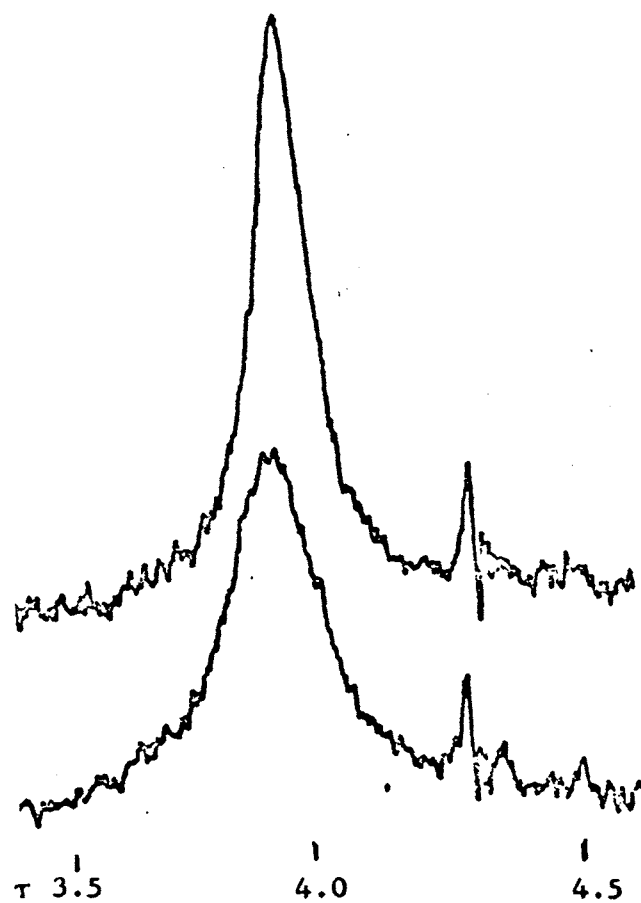


Figure 25. Tropyl Azide in Acetone - 25% Deuterium Oxide at 20° (Bottom Spectra) and at 50° (Top Spectrum).

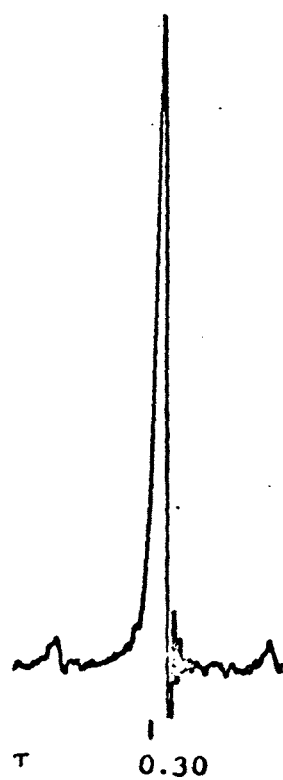


Figure 26. Tropylium Perchlorate in 75% Aqueous Dioxane at 34°.

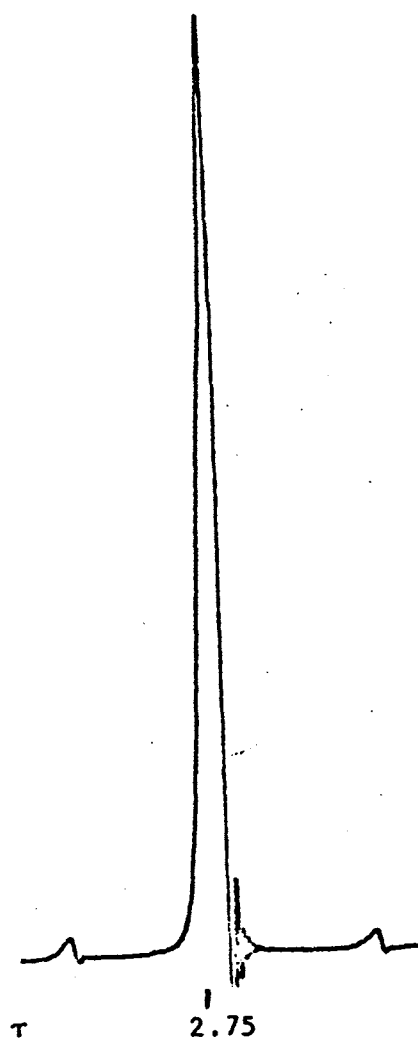


Figure 27. 2% Tropylium Azide - 16% Tropylium Perchlorate in 15% Aqueous Dioxane at 34°.

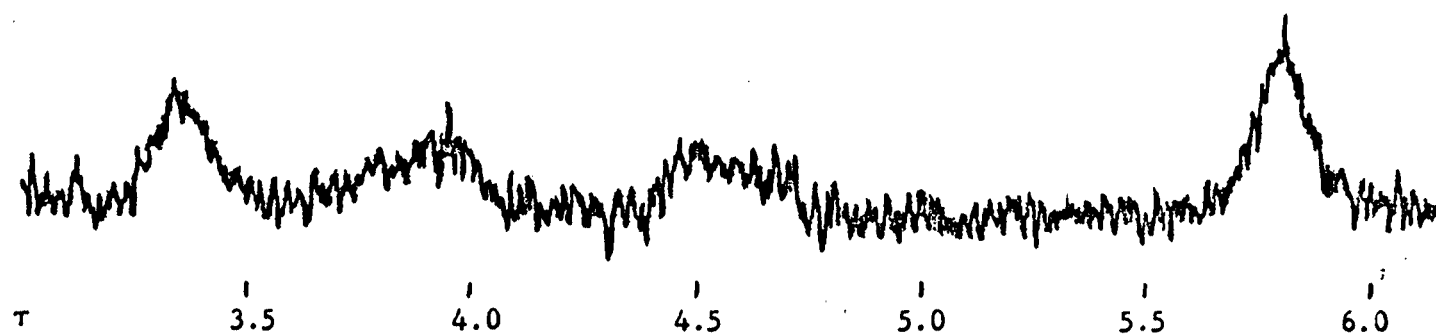
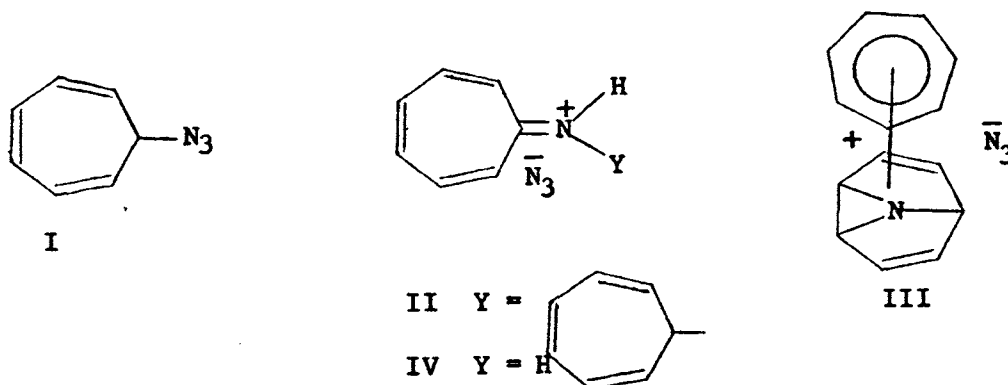


Figure 28. Tropylium Perchlorate and Triethylamine in Acetonitrile at 34°.

IV. SUMMARY

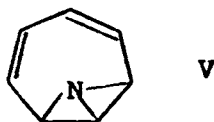
An investigation of the structures of several of the products resulting from the decomposition of troyl azide (I) and of the chemistry of related processes has been undertaken. Irradiation of samples of (I) in the vapor phase with low intensity UV G.E. Sun Lamps furnished a low melting white solid identified as troyl troponimmonium azide (II). Earlier experiments of a similar nature were sporadically reproduced and furnished an isomeric material which was tentatively assigned the structure (III).³ Attempts to isolate the free amine from this compound proved unsuccessful.



Upon standing, solutions of (I) slowly formed troponimmonium azide (IV) in the cold. The structures (II) and (IV) were confirmed by conversion to the corresponding fluoborates and comparison with samples prepared by the methods of Bauld⁸⁶ and Dauben.⁸⁷

Attempts to determine whether any of the bicycloazabutane derivative (V) was present at some stage were undertaken by examining the

reaction mixtures for traces of benzaldimine (an expected rearrangement product of (V)) using 2,4 dinitrophenylhydrazine reagent. These proved unsuccessful when it was determined that troponimines underwent rearrangement under the analysis conditions to furnish the benzaldehyde derivative.



The nature of amine-tropylium ion interactions was investigated. While this study was underway, the dissertation of P. B. Shevlin⁹⁴ appeared. The results reported by Shevlin are at variance with those of D. S. Wulfman¹ and with those obtained in these laboratories as well as those reported by several other workers. We found, in contrast with Shevlin, that tropylium salts form at least 2 and possibly 4 different complexes with pyridine, none of which involves formation of a tightly held sigma complex in which an N-tropyl pyridinium species is present. The activation parameters for the process obtained in these laboratories and at Yale are nearly identical. Similar behavior was noted for 3,5 dimethyl pyridine. With 2 and 4 methylated pyridines, a sigma complex was formed which apparently involves C alkylation. In these instances no evidence of reversible complex formation was observed.

Re-examination of dimethyl sulfoxide as a solvent for such studies reaffirmed the findings of Wulfman that sigma complex formation with solvent molecules occurred and precluded its use for equilibria studies.

In hopes of gaining insight into the amine processes, the synthesis of series of troyl acetates (acetate, chloracetate, dichloracetate) was undertaken. In only the unsubstituted case was any ester formed. In all cases tropone was obtained in fair yield. In only one case was any tropilidene obtained. This suggests that the process proceeds by some other path than the acid catalyzed decomposition of bis-troyl ether.

V. EXPERIMENTAL

All IR spectra were taken on a Beckman IR 5A, Perkin-Elmer 137, or Perkin-Elmer 337. All IR spectra were calibrated with the various bands of polystyrene. All NMR spectra were run on a Varian A56/60 spectrometer and are reported in τ units with tetramethylsilane as the internal standard, or external standard when necessary. All ultraviolet spectra were taken on a Beckman DK2A spectrometer and the solvent used was 99.5% ethanol. All melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Mass spectra were determined on a Consolidated Electrodynamics Corporation model 104 mass spectrometer with a gas chromatographic interface using an electron multiplier and scanning rate of two seconds per octave.

A. Tropylum Perchlorate

Tropylum perchlorate was prepared by the method of Kursanov.^{80,82} Phosphorous pentachloride (450 g, 2.2 moles) was dissolved in 4 liters of refluxing carbon tetrachloride. The resulting solution was cooled and 1 mole (92 g) of redistilled tropylidene (bp 113-114°) was added all at once. The material was stirred for 15 minutes by an overhead stirrer and then allowed to stand overnight at room temperature. Distilled water (165 ml) was then added to the carbon tetrachloride slurry and the two phases stirred until all the tropylum salts went into solution. The aqueous phase was separated and placed in a beaker. Concentrated (70%) perchloric acid

(100 ml) was added slowly to the beaker with stirring. The mixture was cooled to approximately 10°. The tropylium perchlorate slurry was filtered through a fritted glass funnel. The yellowish-white crystals were washed with 50 ml of cold ethanol and then 200 ml of cold diethyl ether. The white crystals isolated at this point usually amounted to an 80 to 85% yield and were moistened with water (2 ml) and stored in plastic bottles. This procedure alleviates the problem of explosions.⁸³ Kursanov obtained a 98% yield on a 0.1 mole scale. The NMR spectrum showed a single peak, in agreement with the literature, in water at τ 0.7.^{80,82}

B. Tropylium Fluoborate

The same procedure as above was used except for the substitution of fluoboric acid for perchloric acid. The fluoborate salt is much more soluble in water so sec-butyl alcohol was added to the aqueous solution to precipitate more of the tropylium fluoborate. The average yield of this preparation was 60%. The Organic Synthesis procedure⁸⁴ gives 80 to 89% yields by a somewhat different procedure. The melting point of the material was 234-235°C. Dauben and co-workers⁸⁵ reported that the fluoborate salt decomposed slowly above 210°C. The NMR spectrum shows a single peak in water at τ 0.7 (lit⁸⁴ τ 0.7).

C. Tropylium Bromide

One mole (92 g) of tropylidene (bp 113-114°) was dissolved in 400 ml of carbon tetrachloride. This solution was placed in a 1 liter round bottom flask which was cooled in an ice bath. One mole

(160 g) of bromine was added to the above stirred solution over a 4-hr. period. The yellow-green solution was then placed on an aspirator and the carbon tetrachloride removed. The residual dark green dibromotropyliene was left connected to the aspirator and heated at 60° for 36 hours. At the end of this time the greenish-black solid was washed with 50 ml of carbon tetrachloride and filtered. The tropylium bromide was washed with an additional 50 ml of carbon tetrachloride and filtered again. This procedure yielded 91 g (53% yield) of yellow tropylium bromide mp 199-201° (lit 201-203°).⁷⁶ Doering and Knox⁶ reported a 60% yield on the same reaction. The NMR spectrum in water shows a single peak at τ 0.7 (lit⁸⁴ τ 0.7).

D. Ditropyl Ether

Tropylium perchlorate (10 g, 0.05 mole) was placed in a separatory funnel containing 200 ml of saturated aqueous sodium bicarbonate solution. The bicarbonate solution bubbled vigorously. The resulting ditropyl ether was extracted with three 100-ml portions of methylene chloride. The methylene chloride solution was dried over 10 g of anhydrous magnesium perchlorate. The methylene chloride was then removed at aspirator pressure to yield 3.9 g (79%) of pale yellow liquid. Doering and Knox⁷¹ obtained an 81% yield for this same reaction. The IR spectrum in carbon tetrachloride had λ_{\max} 3.30 μ (s), 3.35 μ (s), 3.47 μ (w), and 3.52 μ (w) (C-H), 6.11 μ (vs), 6.34 μ (vs), 6.59 μ (s), and 6.80 μ (m) (C-C), 7.00 μ (m), 7.18 μ (m), 7.37 μ (w), 7.82 μ (m), 8.00 μ (m), 8.21 μ (s) (C-O), 9.00 μ (m), 11.23 μ (m), 12.04 μ (s), and 15.29 μ (s). The UV spectrum had

$\lambda_{\text{max}}^{\text{EtOH}}$ 257 nm ($\epsilon = 4,000$). These spectra are in agreement with the literature.^{71,76}

E. Tropylum Chloride

Ditropyl ether (10 g, 0.05 mole) was placed in 50 ml of ethanol in a round bottom flask. The system was saturated with dry hydrogen chloride gas. The reaction was carried out at room temperature under a nitrogen atmosphere. Cold anhydrous diethyl ether (100 ml) was added and pale yellow crystals of tropylum chloride precipitated. These were filtered in a cold fritted glass funnel under a nitrogen atmosphere. The crystals weighed 13.6 g (54% yield). The melting point was 96 to 99° (lit⁷¹ mp 101°). Doering and Knox⁷¹ using a somewhat different preparation obtained a 73% yield.

F. Tropyl Azide

Sodium azide (10 g, 0.15 mole) was combined with tropylum perchlorate (10 g, 0.053 mole) in 100 ml of distilled water in a separatory funnel. The tropyl azide was extracted with four 50 ml portions of methylene chloride. The total methylene chloride solution was dried over anhydrous magnesium perchlorate and the methylene chloride removed at aspirator pressure. The residual tropyl azide (6 g, 0.045 mole) (85% yield) was a clear very pale yellow liquid which has a very pungent, unpleasant odor. Looker⁴ reported a 56% yield and Wulfman⁶⁸ a 95% yield using the same procedure. The tropyl azide was of sufficient purity at this point that it was used without further purification. The IR spectrum in carbon tetrachloride had λ_{max} 3.30 μ (m), 3.35 μ (m) and 3.51 μ (w) (C-H), 4.73 μ

(vs) (N_3), 6.3μ (m), 6.53μ (m), and 7.18μ (s) (C-C), 7.89μ (vs), 8.20μ (m), and 8.95μ (s). The UV spectrum shows $\lambda_{\text{max}}^{\text{EtOH}}$ 255 nm. These are in agreement with the literature.^{1, 4, 68}

G. 3-Bromocycloheptene

3-Bromocycloheptene was prepared by the method of Cope and co-workers.⁹² Cycloheptene (9.6 g, 0.1 mole) was added to a slurry of N-bromosuccinimide (18 g, 0.1 mole) in 150 ml of carbon tetrachloride. A small amount of benzoyl peroxide (0.001 g) was added and the mixture heated to reflux and stirred for 3 hours. At the end of this time all the solid floated which indicated that it was succinimide and that the reaction was over. The slurry was filtered and the carbon tetrachloride removed at aspirator pressure. The residual bromide was a colorless liquid and weighed 15 g (86% yield). Cope and co-workers obtained a 94% yield from the same reaction.⁹² Low resolution and high resolution mass spectra of this compound were completely consistent with the assignment.¹⁰¹

H. 3-Azidocycloheptene

The preparation of 3-azidocycloheptene is an extension of the reactions of 3-bromocycloheptene reported by Hatch and Bachmann.⁹³ A solution of 15 g (0.086 moles) of 3-bromocycloheptene in 100 ml of acetone was prepared. Sodium azide (7.8 g, 0.12 moles) was added to the acetone solution and the slurry stirred for 2 hours at room temperature. The slurry was filtered and the acetone removed at aspirator pressure. The residual 3-azidocycloheptene (6.4 g, 54% yield) was a pale yellow liquid. The IR spectrum in carbon

tetrachloride had λ_{\max} 3.31 μ (w), 3.41 μ (s), and 3.51 μ (m) (C-H), 4.78 μ (s) (N_3), 6.09 μ (vw), 6.21 μ (vw), and 6.91 μ (m) (C=C), 7.40 μ (w), 8.02 μ (s), 8.46 μ (w), 8.75 μ (s), 9.46 μ (w), 9.53 μ (vw), 10.47 μ (w), 11.21 μ (w) and 14.83 μ (m). The NMR spectrum in carbon tetrachloride showed a doublet at τ 4.37 (2H) (olefinic protons), a broad singlet at τ 6.1 (1H) (proton adjacent to azide group), a broad singlet at τ 8.0 (2H) (allylic protons) and a multiplet at τ 8.35 (6H) (other ring protons). Low resolution and high resolution mass spectra of this compound were run and the spectra were completely consistent with the structure assignment.¹⁰¹

I. 3-Aminocycloheptene

A solution of 6.4 g (0.047 mole) of 3-azidocycloheptene in 30 ml of anhydrous methanol was prepared. Platinum oxide (0.15 g) was added to this solution. Excess sodium borohydride was then added and the reaction was allowed to stir for 30 minutes. The platinum metal was removed by filtration. The yellow solution was treated with 1 g of Norit and filtered again to give a colorless solution. One half of the methanol was removed at aspirator pressure and 20 ml of water added. The aqueous solution was extracted twice with 50 ml portions of diethyl ether. The diethyl ether solution was dried over anhydrous magnesium sulfate and the ether removed at aspirator pressure. The residual amine (1 g, 21% yield) had the following IR spectrum in carbon tetrachloride: 2.91 μ (m) (N-H), 3.31 μ 3.43 μ (s), and 3.52 μ (m) (C-H), 6.21 μ (m) (C=C), 7.30 μ (m), 7.39 μ (m), 8.23 μ (m), 9.00 μ (m), 9.22 μ (m), and 9.69 μ (m). Low resolution and high resolution mass spectra of this compound were completely consistent with the structure assignment.¹⁰¹

J. Tropyl Tropone Imine Hydrazoic Acid Salt

Tropyl azide (6 g) was placed in a vacuum system and distilled at less than 3 mm pressure. The vapor passed through a Vycor tube, which was heated and irradiated by two IR heat lamps, and was collected on a liquid nitrogen cold finger. The distillate which consisted of a white solid (25 mg) in the pale yellow tropyl azide was collected and centrifuged. The tropyl azide was removed and the white solid washed three times with 1 ml portions of cold hexane and the hexane was removed with a medicine dropper each time. All of this experiment was carried out in a nitrogen atmosphere. The IR spectrum had λ_{max} 3.37 μ (s), 3.42 μ (s), and 3.49 μ (s) (C-H), 4.74 μ (s) (N_3), 6.90 μ (m) (C=C), 7.03 μ (m), (C=C), 8.91 μ (vs), 9.34 μ (m), and 9.57 μ (w) (-N-), 7.32 μ (w) (N_3), and also 7.98 μ (vs), 11.2 μ (s), 11.27 μ (s) and 11.48 μ (s). The NMR spectrum in acetonitrile shows a strongly coupled multiplet at τ 2.35 which gives the same peak at half the former intensity plus a peak at τ 0.7 (tropylium ion) upon treatment with trifluoroacetic acid. The UV spectrum shows $\lambda_{\text{max}}^{\text{EtOH}}$ 236 nm ($\epsilon = 10,000$), 287 nm ($\epsilon = 2,000$), 317 nm ($\epsilon = 5,000$), and 325 nm ($\epsilon = 5,500$). These are in agreement with the work of Bauld and Rim⁸⁶ and Dauben and Rhoades⁸⁷ for the tropone imine system.

K. Tropone Imine Hydrazoic Acid Salt

A solution of a trace of tropyl tropone imine hydrazoic acid salt in 10 ml of tropyl azide was placed in a freezer at -20° for three days. At this time about 150 mg of yellow solid was in evidence.

This solid was filtered, washed with cold hexane and dried. All the above work was done in a nitrogen filled dry box. The crystals were insoluble in everything but water and strong acids. They darkened at 88-90° and melted at 140-143°. An IR (nujol Mull) spectrum showed peaks at 4.9 μ (m) (N_3), 6.1 μ (w) (C=C), 6.65 μ (m), 6.7 μ (m) (C=C or C=N), 8.0 μ (w), and 12.8 μ (m). The UV spectrum showed $\lambda_{\text{max}}^{\text{EtOH}}$ 236 nm, 316 nm, and 325 nm. The NMR spectrum in d_3 -nitromethane had a narrow multiplet centered at τ 2.35. The solid upon treatment with fluoboric acid in acetonitrile yielded the fluoborate salt of tropone imine. The fluoborate salt melted at 193-195° (lit⁸⁷ mp 192-194°). The hydrazoic acid salt of tropone imine forms a picrate which melts 194-195° (dec).

L. Tropone Imine Hydrozoic Acid Salt

Tropyl azide (10 g) was placed in a sealed container under nitrogen and kept in a freezer at -20° for 10 days. At the end of this time the tropyl azide was a reddish brown color and contained a small amount of pale yellow crystalline needles. These crystals were filtered, washed with benzene and dried in a nitrogen filled dry box to yield about 200 milligrams. These crystals were identified by their melting point and IR, NMR, and UV spectra as tropone imine hydrazoic acid salt.

M. Hydrogenation of Tropone Imine Hydrazoic Acid Salt

An approximately 10% solution of the hydrazoic acid salt of tropone imine in 1 ml of tropyl azide was dissolved in 30 ml of ethanol containing 0.2 g of platinum oxide. Sodium borohydride (0.5 g) was added to this solution and the flask placed on an atmospheric

pressure hydrogenation system. The solution was stirred until hydrogen uptake ceased. The platinum was removed by filtration. The ethanol was then removed at aspirator pressure. A residual white solid remained. This was assumed to be a boron-nitrogen complex. It was treated with 20 ml of water and extracted with two 25 portions of benzene. The benzene was then distilled down to a total residual volume of 2 ml. A GC spectra showed two major peaks and one minor peak as well as benzene. The three components were identified by mass spectral analysis. The two major peaks were cycloheptane and 3-aminocycloheptene. The minor peak was cycloheptyl-amine. The interpretations were made on the basis of information in H. Budzikiewicz, C. Djerassi, and D. Williams, 'Interpretation of Mass Spectra of Organic Compounds', Holden-Day Inc., San Francisco, 1964 and by comparison with authentic samples of the amines. The sample of 3-aminocycloheptene was prepared as described earlier. The cycloheptylamine and cycloheptane were purchased from Aldrich Chemical Company and were shown to be pure by gas chromatography.

N. Tropyl Methyl Ether

Tropyl methyl ether was prepared by the method of Medz.⁸⁸ Sodium metal (6.9 g, 0.3 g-atom) was added to 250 ml of anhydrous methanol in a 500 ml round bottom flask equipped with a reflux condenser and cooled in an ice bath over a period of one hour. Tropylium perchlorate (38.2 g, 0.2 mole) was added to the methanol solution at this time. The resulting slurry was stirred at room temperature for 90 minutes. The mixture was then placed on an aspirator and concentrated down to one half its original volume. Diethyl ether (300 ml)

was added to the residual methanol solution. The diethyl ether solution was then extracted with three 100-ml portions of water. The combined aqueous extract was back extracted with 100 ml of diethyl ether. The total diethyl ether solution was then extracted with two 100-ml portions of saturated aqueous sodium chloride solution. The ether solution was dried over 15 g of anhydrous magnesium sulfate for 30 minutes. The diethyl ether was removed at aspirator pressure. The residual tropyl methyl ether (12 g, 50% yield) was an oily very pale yellow liquid. Medz⁸⁸ reported a 98% crude yield for the same procedure. The IR in carbon tetrachloride had λ_{\max} 3.34 μ (s), 3.45 μ (s), and 3.55 μ (m) (C-H), 6.20 μ (m), 6.51 μ (m) and 6.90 μ (m) (C=C), 7.10 μ (m), 7.20 μ (s), 7.65 μ (m), 8.27 μ (vs) (C-O), 9.07 μ (vs), 10.11 μ (s), 11.02 μ (w), and 12.01 μ (w). The NMR spectrum showed a multiplet at τ 3.75 (2H), a multiplet centered at τ 4.26 (2H), a quartet centered at τ 4.91 (2H), a singlet at τ 7.17 (3H), and a triplet at τ 8.17 (1H). These spectral characteristics were in agreement with those of Medz.⁸⁸

O. Methyl Tropylidene

Methyl tropylidene was prepared by the method of Medz.⁸⁸ Magnesium metal (4.14 g, 0.17 g-atom) was placed in a 500 ml round bottom flask containing 250 ml of diethyl ether. Methyl iodide (24.5 g, 0.17 mole) was added to the solution over a 45 minute period. The Grignard reaction started immediately and proceeded smoothly. After 45 minutes the solution was dark gray and no magnesium metal was in evidence. Tropyl methyl ether (15.5 g, 0.13 mole) in 50 ml

of diethyl ether was added to the stirred solution over a period of 45 minutes. A bright orange color formed upon addition of each drop and then disappeared. After all the tropyl methyl ether had been added, 50 ml of 2N hydrochloric acid was added slowly. The aqueous phase was dark yellow at this point and the ether phase was light yellow. The ether phase was separated and dried over anhydrous magnesium sulfate. The diethyl ether was removed by aspirator. The residual methyl tropylidene (7.7 g, 56% yield) was a light yellow liquid. Medz⁸⁸ reports a 91.5% crude yield for the same preparation. The NMR spectrum shows a multiplet centered at τ 3.67 (2H), a multiplet at τ 4.10 and another at τ 4.30 (2H), a doublet centered at τ 5.22 and another at τ 5.38 (2H), a multiplet centered τ 8.75 (1H), and a singlet at τ 9.08 (3H). The IR spectrum in carbon tetrachloride had λ_{\max} 3.32 μ (s), 3.40 μ (s), 3.51 μ (s) (C-H), 6.21 μ (w), 6.27 μ (w) and 6.90 μ (s) (C=C), 7.17 μ (m), 7.29 μ (s), 7.75 μ (m), 8.39 μ (w), 9.43 μ (s), 9.84 μ (s), 10.56 μ (w), and 11.71 μ (w). These spectral characteristics are in agreement with those in the literature.⁸⁸

P. t-Butyl Chloride

tert-Butyl alcohol (111 g, 1.5 moles) was placed in a separatory funnel. Concentrated hydrochloric acid (400 ml) was added to the alcohol. The separatory funnel was then shaken until the two layers remained clear. The tert-butyl chloride was separated, washed twice with 100 ml portions of 5% sodium bicarbonate solution, once with 150 ml of water and then dried over anhydrous magnesium sulfate.

The material was then distilled (bp 51-52°). A total of 126 g (91% yield) of the product was collected. The boiling point, and NMR spectra were in agreement with the assignment. The NMR spectrum showed a single peak at τ 8.77.

Q. t-Butyl Tropylidene

tert-Butyl tropylidene was prepared by the method of Medz.⁸⁸ Magnesium metal (36 g, 1.5 moles) was placed in a two liter round bottom flask containing 500 ml of anhydrous diethyl ether. tert-Butyl chloride (138 g, 1.5 moles) was added to the flask over a period of one hour. The reaction started almost immediately and proceeded smoothly. The solution of Grignard reagent was gray at the end of the addition. Tropyl methyl ether (70 g, 0.57 moles) was added to the stirred Grignard reagent solution over a period of one hour. At this time 100 ml of 15% hydrochloric acid was added slowly to destroy the magnesium salts. Water (100 ml) was then added to the flask. The diethyl ether solution was separated, washed with 10% potassium carbonate solution (50 ml) and water (50 ml). It was then dried with anhydrous magnesium sulfate. The diethyl ether was removed at aspirator pressure. The t-butyl tropylidene was distilled (bp 55-56° @ 1 mm) (lit⁸⁸ bp 85-85.5 @ 25 mm) to yield 26 g (31% yield). Medz⁸⁸ reported a 39% yield. Spectral characteristics were in agreement with those in the literature.⁸⁸ The UV spectrum showed $\lambda_{\text{max}}^{\text{EtOH}}$ at 257 nm. The NMR spectrum in carbon tetrachloride showed a triplet at τ 3.40 (2H), a multiplet at τ 3.97 (2H), a quartet at τ 4.79 (2H), a triplet at τ 8.93 (1H), and a singlet at τ 9.03 (9H).

R. t-Butyl Tropylium Perchlorate

Phosphorus pentachloride (45 g, 0.22 mole) was added to 400 ml of carbon tetrachloride in a round bottom flask. This slurry was heated until all the phosphorus pentachloride dissolved. tert-Butyl tropyliidene (14.8 g, 0.1 mole) was added all at once to the flask. The mixture was then allowed to stand at room temperature for 90 minutes. Then 14 ml of water was added to the slurry and the two phases stirred until all the tert-butyl tropylium ion dissolved in the aqueous phase. The aqueous phase was separated and 10 ml of 70% perchloric acid added to it. The aqueous solution was cooled in an ice bath and 10 ml of tert-butyl alcohol added to it. White solid precipitated immediately. This was filtered and washed with 10 ml of cold diethyl ether. White crystals of t-butyl tropylium perchlorate (16 g, 64% yield) were obtained. Medz obtained a 4.5% yield by a somewhat different procedure.⁸⁸ Spectral properties are in agreement with those in the literature.⁸⁸ The NMR spectrum in deuterium oxide containing one drop of trifluoroacetic acid shows a singlet at τ 0.55 (6H), and a singlet at τ 7.93 (9H).

S. t-Butyl Tropylium Azide

A slurry of 16 g (0.067 mole) of t-butyl tropylium perchlorate in 100 ml of distilled water was placed in a separatory funnel. Sodium azide (10 g, 0.15 mole) was added to the separatory funnel. The resulting t-butyl tropylium azide was extracted with two 100 ml portions of diethyl ether. The diethyl ether solution was dried over anhydrous magnesium sulfate. The diethyl ether was removed by

an aspirator. The residual yellow oil weighed 6.5 (52% yield).

The IR spectrum of the material showed peaks at 3.34 μ (s), 3.43 (s), and 4.51 μ (m) (C-H), 4.73 μ (s) (N_3), 6.04 μ (m), 6.87 μ (m), and 7.12 μ (m) (C=C). The NMR spectrum showed a broad multiplet centered at τ 3.5 (4H) (1,6,2, and 6 hydrogens), a multiplet centered at τ 4.5 (2H) (3,4 hydrogens), a multiplet centered at τ 6.46 (1H) (7 hydrogen), and a sharp singlet at τ 8.75 (9H) (t-butyl group).

T. Photolysis of t-Butyl Tropyl Azide

The t-butyl tropyl azide (6.5 g) was photolyzed with two IR lamps in the same manner as tropyl azide. The distillate was a yellow liquid. However its NMR spectrum was nearly identical with the spectrum of the starting material and the other properties appeared to be the same. It was assumed that no reaction occurred and this preparation was discarded.

U. Ditropylamine

Ditropylamine was prepared by the method of Doering and Knox.⁷⁶ Tropylum perchlorate (19.1 g, 0.1 mole) was placed in a separatory funnel with 200 ml of ammonium hydroxide. The resultant ditropylamine was extracted with four 125 ml portions of pentane. The pentane solution was dried over anhydrous magnesium sulfate and concentrated to approximately 50 ml total volume. The solution was placed in a freezer at -20° for one hour. The ditropylamine crystallized to give 6.9 g (70% yield)(lit⁸⁷ 60%) of pale yellow crystals (mp $28-29^\circ$ (lit⁸⁷ mp 30°). The IR, NMR, and UV spectra were in agreement with those in the literature.⁸⁷ The NMR spectrum in carbon tetrachloride showed a triplet at τ 3.4 (2H), a multiplet centered

at τ 3.93 (2H), a quartet centered at τ 4.72 (2H), and a triplet at τ 8.10 (1H). The IR spectrum (neat) showed peaks at 3.5μ (m) (N-H), 3.45μ (s), 3.60μ (m), and 3.71μ (m) (C-H), 6.18μ (m), 6.57μ (m), 6.88μ (m) (C=C), 7.18μ (s), 7.41μ (w), 7.71μ (m), 7.90μ (w), 8.41μ (m), 8.86μ (s), 9.40μ (w) and 9.88μ (s).

V. Tropyl Tropone Imine Fluoboric Acid Salt

This salt was prepared by the method of Bauld.⁸⁶ Tropylium fluoborate (2.7 g, 0.015 mole) was placed in a flask with 100 ml of acetonitrile and 3 g (0.015 mole) of ditropylamine. The solution was refluxed for 10 minutes and then cooled in an ice bath. The acetonitrile was then removed on an aspirator until the total volume was about 6 ml. Cold diethyl ether (35 ml) was added at this point to precipitate 1.6 g (39% yield) of troyl tropone imine fluoboric acid salt as tan crystals. The melting point was 112-114° (lit⁸⁷ mp 109°). The spectral properties were in agreement with those in the literature.⁸⁷ The NMR spectrum in acetonitrile showed a multiplet at τ 2.35 (6H), a triplet at τ 3.18 (2H), a multiplet at τ 3.56 (2H), a quartet at τ 4.46 (2H), and a triplet at τ 6.00 (1H).

W. Tropone Imine Fluoboric Acid Salt

Tropyl tropone imine fluoboric acid salt (2 g, 0.007 mole) was placed in a flask with 15 ml of ethanol and the solution refluxed for 15 minutes. The ethanol solution was then concentrated to about 3 ml on an aspirator. Cold diethyl ether (20 ml) was added to the ethanol solution to precipitate 0.9 g (66% yield) of yellow crystals

of tropone imine fluoboric acid salt. Dauben and Rhoades⁸⁷ reported a 66% yield of white crystals for the same reaction. The NMR and UV spectra were in agreement with those in the literature.⁸⁷ The melting point of the solid was 193-195° (lit⁸⁷ mp 192-194°). The UV spectrum showed $\lambda_{\text{max}}^{\text{EtOH}}$ 324 nm, 314 nm (sh), 239 nm (sh), and 234 nm. The NMR spectrum shows a multiplet at τ 2.28.

X. The Dinitrophenylhydrazone From Tropone Imine

Tropone imine fluoboric acid salt (1 g) was added to 100 ml of saturated aqueous potassium bicarbonate solution. The resulting tropone imine was extracted with three 100 ml portions of diethyl ether. The diethyl ether solution which was a bright orange color was dried over 10 g of anhydrous magnesium sulfate. Ethanol (5 ml) was then added to the diethyl ether solution and the diethyl ether removed on an aspirator. When the total volume of the solution was about 4 ml the solution was added all at once to 10 ml of 0.1 M 2,4 dinitrophenylhydrazine in ethanol and phosphoric acid.¹⁴ After three minutes a brown solid began to form. It was filtered after 10 minutes additional time and air dried. The brown solid was recrystallized from ethanol to give an orange solid. The melting point and mixed melting point with authentic benzaldehyde dinitrophenylhydrazone was 234-236°.⁸⁶

Y. The Dinitrophenylhydrazone From Tropone Imine

Tropone imine hydrazoic acid salt (250 mg) was added to 50 ml of aqueous saturated potassium bicarbonate solution. The resulting tropone imine was extracted with 150 ml of diethyl ether. The diethyl

ether solution was dried over anhydrous magnesium sulfate. The diethyl ether solution was bright orange at this time. Ethanol (3 ml) was added to the solution and the diethyl ether removed at aspirator pressure. The total solution of about 2 ml was added to 10 ml of 0.1 M 2,4 dinitrophenylhydrazine in ethanol and phosphoric acid.¹⁴ After a few minutes an orange solid precipitated. It was filtered and air dried. It was then recrystallized from ethanol to yield a bright orange solid. The melting point and mixed melting point with the dinitrophenylhydrazine of benzaldehyde was 234-236°. ~~6~~

2. Tropyl Acetate

Tropylum perchlorate (20 g, 0.1 mole) was mixed with 50 ml of aqueous saturated potassium acetate solution. This was stirred for 10 minutes and became a slurry containing large amounts of white solid. Methylene chloride (450 ml) was mixed with the slurry and the entire mixture filtered. The methylene chloride solution was separated and dried over anhydrous magnesium perchlorate. The methylene chloride was removed at aspirator pressure and the residue vacuum distilled. This distillation yielded a pale yellow liquid (bp 32-33° @ 0.1 mm). An NMR spectrum showed a broad singlet at τ 3.02 (tropone), a triplet at τ 3.35 (2H), a multiplet centered at τ 3.88 (2H), a quartet centered at τ 4.53 (2H), a triplet centered at τ 5.11 (1H), and a singlet at τ 8.10 (3H). From this spectrum it appeared that the reaction gave tropone (0.5 g, 4.7% yield) and tropyl acetate (1.5 g, 11% yield).

AA. Attempted Preparation of Tropyl Chloroacetate

Tropylum perchlorate (10 g, 0.05 mole) was mixed with a solution of potassium chloroacetate (47 g, 0.5 mole) in 50 ml of water. This

slurry was mixed with 450 ml of methylene chloride. The total slurry was shaken for 5 minutes and then filtered. The methylene chloride solution was separated and dried over anhydrous magnesium perchlorate. The methylene chloride was removed at aspirator pressure and the residue vacuum distilled. The only two products isolated were tropyliene (1.3 g, 14% yield) and tropone (2.8 g, 25% yield). The tropyliene showed peaks in the IR spectrum at 3.34μ (s), 3.38μ (s), 3.46μ (s), 3.46μ (s), and 3.51μ (s) (C-H), 6.08μ (m), and 6.97μ (m), 9.57μ (w), 9.84μ (w), 10.57μ (w), 11.13μ (w). The UV spectrum shows $\lambda_{\text{max}}^{\text{EtOH}}$ at 2.55 nm. The tropone (neat) shows a single peak in the NMR spectrum at τ 3.02. The UV spectrum of tropone had $\lambda_{\text{max}}^{\text{EtOH}}$ at 310 nm (sh), 300 nm, 233 nm, 228 nm, and 224 nm. These are in agreement with the spectral characteristics in the literature.^{12,13} The same reaction was run in acetonitrile as the solvent, and equimolar amounts of tropylium perchlorate and "dry" potassium chloroacetate. The slurry was stirred for 30 minutes at room temperature and filtered. The acetonitrile was removed at aspirator pressure and the residue vacuum distilled. The only product isolated was tropone in 31% yield.

BB. Attempted Preparation of Tropyli Dichloroacetate

Tropylium perchlorate (10 g, 0.05 mole) was mixed with 83 g (0.5 mole) of potassium dichloroacetate in 50 ml of water. Methylene chloride (500 ml) was added and the entire slurry was shaken for 5 minutes and then filtered. The methylene chloride solution was separated and dried over anhydrous magnesium perchlorate. The

methylene chloride was removed at aspirator pressure and the residue vacuum distilled. The only product isolated was tropone (1.9 g, 18% yield).

CC. Preparation of Samples for NMR Studies

The samples of tropylium ion for NMR study were all prepared in the same way. Tropylium perchlorate (0.10 g) was placed in an NMR tube and 0.90 g of the amine added to it. The tube was then purged with dry nitrogen gas and capped. The only exception to this was the solution of tropylium ion in d_5 -pyridine which was added to an equal amount of acetone for the studies of tropylium ion and pyridine in acetone. All solvents were Reagent Grade or Spectral Grade quality.

DD. Measurements of Variable Temperature NMR Spectra

The variable temperature NMR spectra were measured with a Varian Associates A 56/60 NMR spectrometer. The temperature was controlled with a Varian model V6040 temperature controller. Nitrogen gas was passed through a cooling coil immersed in liquid nitrogen to cool the probe to the desired temperature. The temperature was found to be accurate to $\pm 1^\circ$ through calibrations using methanol as the standard.

VI. APPENDICES

APPENDIX I

THE NONEXISTENCE OF TROPYLIUM ANALOGS OF THE
METALLOCENES: TROPYL SELENIDE AND TROPYL TELLURIDE

Senior Research Report, J. J. Ward, 1965

THE NONEXISTENCE OF TROPYLIUM ANALOGS OF THE
METALLOCENES: TROPYL SELENIDE AND TROPYL TELLURIDE

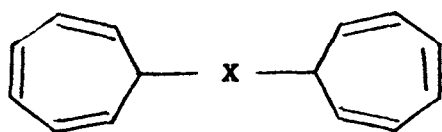
Senior Research Report, J. J. Ward, 1965

Between 90 and 100 kilocalories of stabilization energy is supposedly lost when two moles of tropylium ion react to form covalent materials such as ditropyl amine and ditropyl ether (1). It would appear to be possible to prepare tropylium derivatives analogous to the cyclopentadienyl metallocenes and retain some of this energy. No compounds of this type have been reported.

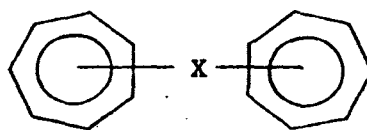
The choice of heteroatoms is limited by the requirement of generating seven equivalent orbitals rather than the five employed in metallocene bonding. The only elements furnishing divalent anions which would appear to be favorable for such bonding would be selenium with empty 4f orbitals and tellurium with empty 5f orbitals. Attempts to synthesize ditropyl selenide and ditropyl telluride by electrolysis of tropylium fluoborate using selenium or tellurium cathodes failed to furnish the desired compounds but did furnish complex mixtures of highly odoriferous materials. Methatheses of the corresponding sodium salts with tropylium fluoborate in a manner analogous to that of Brandsma and Wijers (2) furnished ditropyl selenide and ditropyl telluride.

Nuclear Magnetic Resonance studies established that the compounds were of the structural type I and not II. Studies on the crude and purified oils failed to show the presence of any material possessing 14 equivalent protons. The spectra were typical of substituted

tropylidenes. A plot of the chemical shifts of the C_7 Hydrogens versus the Huggins Electronegativities (3) gave a good straight line for the series ditropyl sulfide, ($\tau = 6.72$) ditropyl selenide ($\tau = 6.83$) and ditropyl telluride ($\tau = 7.10$). The only feature of special note was that the extremely complex spectrum normally associated with the 1,6 hydrogens of tropylienes was resolved in the case of ditropyl telluride ($\tau = 4.59$), into an equally spaced sextet of intensities (1:1:2:2:1:1) ($J=4.5$ c.p.s.). The C_7 Hydrogen resonance for the ether falls at $\tau = 6.52$ rather than 5.63 as would be predicted on the basis of the electronegativities of oxygen.



I



II

Failure to form compounds of the Type II can be attributed to a lack of suitable hybrid orbitals possessing the proper symmetry or to the lack of sufficient stabilization of Type II compounds over Type I. This last factor involves both the magnitude of the resonance energy of tropylium ion and the energy of the required molecular orbitals. Turner (1b) has suggested that the one electron delocalization energy of tropylium ion (2.99β) is expended doing electrostatic work, and has estimated that tropylium ion is of lower stability than benzyl carbonium ion (both in acetic acid). If this is actually the case, very little energy would be available for formation of high energy hybrid orbitals and compensation would rest solely on the possibility of increased delocalization in the sandwich type product.

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APPENDIX II

1-AZATRICYCLO(3,3,0,0²,8) OCTA-3,6-DIENE

D. S. Wulfman and J. J. Ward, Chem. Commun., 267, (1967)

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1-Azatricyclo[3,3,0,0^{2,8}]octa-3,6-diene

By D. S. WULFMAN and J. J. WARD

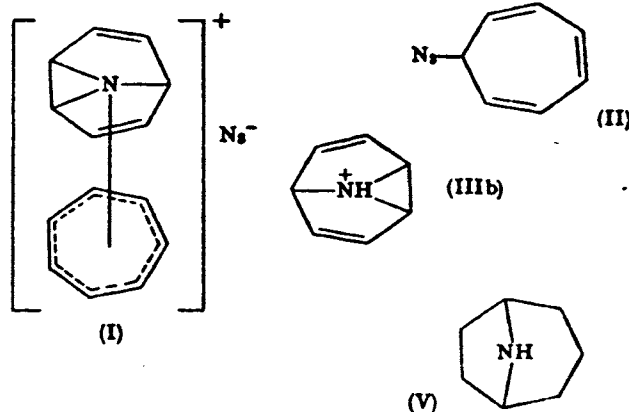
(Department of Chemistry, University of Missouri at Rolla, Rolla, Missouri 65401)

PREVIOUSLY¹ we reported studies dealing with the formation of tropylium-azide ion pair from troyl azide.¹ The structure of the ion-pair appeared to be an open-faced sandwich. It was not possible to tell whether the azide part was perpendicular or parallel to the plane defined by the tropylium ion.

All n.m.r. spectra observed showed a single sharp resonance signal at τ 4.40 (τ 5.20 neat) accounting for 2–3% of the total signal. This signal was τ 0.06 up-field from the centre of gravity of the troyl azide spectrum. We now assign the source of this signal as being due to the novel sandwich compound (I), resulting from the interaction of troyl azide (II) and 1-azatricyclo[3,3,0,0^{2,8}]octa-3,6-diene (IIIa). Treatment of (I) with trifluoroacetic acid furnishes tropylium ion and the ion (IIIb) as is shown by a decrease in the intensity of the resonance signal at τ 4.40* to one half and generation of a new signal at τ 0.73 [the location of the resonance of tropylium fluoroborate in the same solvent, CD_3CN , is τ 0.73] and a peak of variable position and intensity (a function of temperature and of the amount of trifluoroacetic acid) which we ascribe to $\equiv\text{N}^+-\text{H}$, HN_3 , and $\text{CF}_3\text{CO}_2\text{H}$.

The n.m.r. spectrum of (I) is extremely complex at -20° (13 peaks in 7 c./sec.) but on warming to room temperature has the appearance of a 3:2:2 system which is partially resolved with difficulty. Above 60° we have been able to observe only a single resonance.

At least 36 compounds might result from the reactions of troyl azide with itself or from unimolecular processes. These include 1,3-dipolar



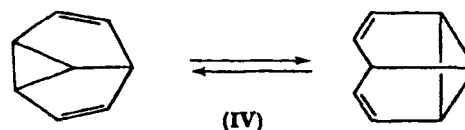
* Determined on a Varian A56—60 n.m.r. spectrometer at 60 Mc./sec. with tetramethylsilane as internal standard in trideuteromethyl cyanide.

addition-type products,² with or without subsequent loss of nitrogen and nitrene reaction³ products, and their possible valence isomerization products followed by possible interaction with troyl azide. Of the structures considered, only (I) is consistent with the i.r., u.v., and n.m.r. spectral data. Comparison spectra have been examined in all cases by using troyl azide, bistroyl ether, troylidene, troylium fluoroborate, and troylium perchlorate.[†] The compound to which we assign the structure (I) possesses many spectral properties in common with these compounds except that the dissimilarities clearly preclude the presence of a free troylium unit or the presence of a simple troyl system. The u.v. spectra show λ_{\max} (EtOH) 236 (ϵ 10,000), 326 (ϵ 5600), and λ_{\max} 287 m μ (ϵ 2200) whereas troyl compounds and troylium ion show λ_{\max} (EtOH) in the range 250–265 m μ (ϵ ~12,000–20,000).⁴ However, the presence of a shoulder at 247 m μ (ϵ 8000) of approximately the same normalized intensity (16,000) as troyl compounds suggests the presence of such a structural unit. The i.r. does not show any C=C stretching characteristic of troylidene or troyl azide. Experiments with troyl azide show only a slight up-field shift in the proton resonance signal after treatment with tertiary amines. The single n.m.r. signal from troylium perchlorate upon treatment with pyridine shifts from τ 0.73 to 4.35. When amines such as trimethylamine are used, a complex n.m.r. spectrum with multiple troylium resonances occurring between τ 3.33 and 5.93 results.⁵ The n.m.r. spectrum of (I) is not inconsistent with these observations but would seem to indicate the existence of rather special conditions to permit complex formation between (II) and (IIIa).

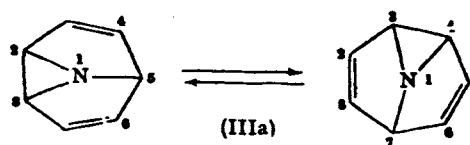
The n.m.r. spectral properties of (I) and (IIIa) and (IIIb) are highly suggestive of ready exchange and valence isomerization reactions.⁶ It seems unlikely the 14 protons of (I) and the 7 C-H protons of (IIIa) and (IIIb) fortuitously occur at the same field strength.

It appears that (I) actually exists as a sandwich ion with or without the azide ion in close proximity but with at least time-average equivalence of both carbon rings. In (IIIa) and (IIIb) it appears that in contrast to tricyclo[3,3,0,0²,³]octa-3,6-diene the valence isomerization process is not limited to the now classic homotroylidene rocking-type Cope

rearrangements⁷ (Scheme 1) but actually involves a hitherto unknown precessional or rotational-type Cope rearrangement (Scheme 2).



SCHEME 1



SCHEME 2

The u.v. spectrum is consistent with this assignment. The absorption maximum at 326 m μ is only present when the ring nitrogen bears a positive charge. This appears to be associated with interaction of the lone pair sp^3 - σ^* orbital with the $4/\pi$ orbitals of the carbonoid system. The broad absorption maximum at 235 m μ is much more intense than that observed by Zimmermann⁸ for tricyclo[3,3,0,0²,³]octa-3,6-diene but falls at the same position. The disappearance upon acid treatment of the 326 m μ absorbance and shifting to maxima at 320 (ϵ 2500), 307 (ϵ 4100), and 293 m μ (ϵ 4200) appears to be the result of the more ready interaction between the nonbonded electron pair of nitrogen and the π -electrons of the two carbon-carbon double bonds.

Catalytic reduction of (I) over Adams catalyst at atmospheric pressure in absolute ethanol furnished a mixture which contained large amounts of cycloheptane and nortropane (V). Verification of the structure of (V) was accomplished by mass spectral analysis[‡] (m/e , 111, 97, 96, 94, 91, 83, 82, 81, 80, 79, 67, 55, 43, 41, 39, 30, 29 amongst others). In addition small quantities of cycloheptyl amine were also obtained and verified mass spectrometrically. In addition, (I) should have a cryoscopic molecular weight of 119, we found 126 ± 15 .[§] Attempts to determine the percentage of ionic azide⁹ were frustrated by the instability of

[†] Test performed for D.S.W. by Hercules Inc., Bacchus, Utah, show dry troylium perchlorate to be at least three times as sensitive to impact as nitroglycerin.

[‡] Mass spectra were determined on a Consolidated Electrodynamics Corporation model 104 mass spectrometer with a gas chromatographic interface using an electron multiplier and scanning at 2 sec./octave. Interpretations were made on the basis of information in H. Budzikiewicz, C. Djerassi, and D. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day Inc., San Francisco, 1964.

[§] Cryoscopic measurements were obtained using redistilled cyclohexanol.

the solid salt. Spectrophotometrically-obtained values ran 30—40% below theoretical.

Compound (I) was prepared at a low conversion (2—3%) by slow evaporation through a (75 cm. \times 2.5 cm.) Vycor tube irradiated with G.E. Sunlamps at pressures below 3 mm. and collection of the distillate on a liquid nitrogen cold finger. Transfer and warming to 0° was carried out under a dry nitrogen atmosphere and (I) was isolated by trituration with cold pentane and centrifugation. Yields at this stage were 10—12 mg. per 8 g. of (II).

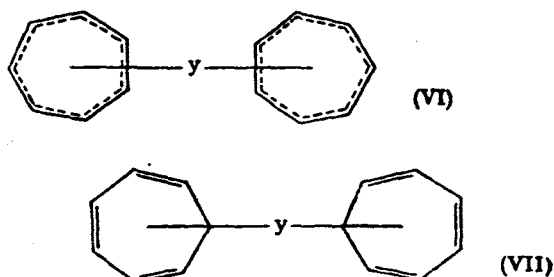
The i.r. spectrum of (I) showed peaks at 2976 s, 2857 s, 2110 s, 1449 m, 1418 m, 1368 w, 1253 vs, 1121 vs, 1081 m, 1046 mw, 894 s, 889 s, 873 s, 694 vs cm^{-1} in CH_2Cl_2 .

The possibility that other tropylium ion derivatives might exist in the form (VI) was investigated for the series^{10,11} $y = \text{O}, \text{S}, \text{Se}, \text{and Te}$. All of these compounds exist solely in the form (VII) and the only thing noteworthy about these compounds is that the C-7 proton resonance in the oxygen compound is τ 0.96 up-field from the position predicted on the basis of Huggin's electronegativities¹² and the C-6—C-1 proton resonances of the tellurium compound, unlike

other tropyliene derivatives, are nicely resolved into a 1:1:2:2:1:1 sextet.

Work is currently under way to establish the exact structure of (I) by X-ray analysis and to determine unequivocally the character and energetics of the isomerization processes involving (I), (IIIa), and (IIIb).

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¹ This Communication is the third in a series on "Tropylidene derivatives"; previous parts C. E. Wulfman, F. Yarnell, and D. S. Wulfman, *Chem. and Ind.*, 1960, 1440; D. S. Wulfman, L. J. Durham, and C. E. Wulfman, *ibid.*, 1962, 859.

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⁴ For tabulations of tropylium and tropylidene spectra see: T. Nozoe, "Non-Benzenoid Aromatic Compounds," ed. D. Ginsberg, Interscience, New York, 1959, p. 344, and G. Berson and R. Willcott, *tert.*, *Rec. Chem. Prog.*, 1966, 27, 139.

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¹¹ By method similar to L. Brandsma and H. J. Wijers, *Rec. Trav. chim.*, 1963, 82, 68.

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APPENDIX III

ATTEMPTED ISOLATIONS OF 1-AZATRICYCLO (3,3,0,0²,8)
OCTA-3, 6-DIENE

ATTEMPTED ISOLATIONS OF 1-AZATRICYCLO (3,3,0,0^{2,8})
OCTA-3, 6-DIENE

Original Isolation of Free Amine

About 500 milligrams of a white solid was filtered away from 20 ml of tropylium azide which had been thermolyzed with infrared lamps in the vapor phase six times. The white solid was placed in a separatory funnel which contained 100 ml of aqueous saturated sodium carbonate solution. This was shaken vigorously and the water-insoluble, organic-soluble material extracted with two 50 ml portions of methylene chloride. The methylene chloride was extracted with 25 ml of 5% sulfuric acid solution. The acidic solution was neutralized with solid sodium carbonate. The neutral solution was extracted with 50 ml of methylene chloride. This acid-base treatment was repeated twice. The final methylene chloride solution was dried over anhydrous magnesium perchlorate and stored under nitrogen until used. This furnished about 45 mg of oil and was subjected to mass spectral analysis and furnished 2-3 mg of a picrate having mp = 192-194. The sample was contaminated with considerable ditropylium ether as revealed by the mass spectrum and the IR spectrum.

The IR spectrum of the mixture in methylene chloride showed the following peaks: 2.38 μ (s), 3.28 μ (s), 3.36 μ (s), 4.34 μ (w), 5.84 μ (m), 6.31 μ (s), 7.04 μ (s), 7.83 μ (s), 8.02 μ (s), 8.21 μ (m), 9.00 μ (s) and 11.21 μ (s).

The UV spectrum in ethanol showed λ_{max} at 312 nm ($\epsilon = 3,000$), 303 nm ($\epsilon = 3,000$), 240 nm ($\epsilon = 7,500$), 232 nm ($\epsilon = 10,000$), 228 nm ($\epsilon = 11,500$), 225 nm ($\epsilon = 11,600$), 222 nm ($\epsilon = 12,000$). The ether

present exhibits absorption over the range 200-260 nm.

Attempted Isolation of Free Amine Using Sodium Sulfide

About 250 milligrams of a white solid was filtered away from 20 ml of troyl azide which had been thermolyzed six times with IR lamps for 12 hours. The solid was mixed with 25 ml of aqueous saturated sodium sulfide solution in a separatory funnel. The aqueous solution was then extracted with 100 ml of methylene chloride. The methylene chloride solution was separated and extracted with 25 ml of 5% hydrochloric acid. The acidic solution was separated and neutralized with solid sodium carbonate. When basic to litmus (the solution goes from pale yellow to strongly yellow) the solution was extracted with 50 ml of methylene chloride. This acid-base technique was repeated six times. The final methylene chloride solution was dried over anhydrous magnesium perchlorate. The methylene chloride was removed until the total volume reached ca. 1 ml. More highly concentrated solution furnished only highly insoluble material. Only a typical troylidene NMR was observed contaminated with a trace of methylene chloride. Approximately 20 mgs of this material was obtained.

Attempted Isolation of Free Amine With Potassium Bromoplumbate

A saturated aqueous solution of potassium bromoplumbate (25 ml) was mixed with 300 milligrams of a white solid obtained from 15 ml of troyl azide which had been irradiated in the vapor phase six times (12 hrs.). This solution was allowed to stand overnight under nitrogen at -20° . The mixture was filtered and the filtrate extracted with 50 ml of methylene chloride. The methylene chloride was dried over

anhydrous magnesium perchlorate. The methylene chloride was removed at aspirator pressure. Nothing remained in the flask.

Attempted Isolation of Free Amine By Distillation

A sample of tropylium azide (10 ml) which had been irradiated five times (10 hrs.) was placed on a vacuum system. The sample was frozen in liquid nitrogen and the pressure reduced to 0.01 mm Hg. The sample was allowed to warm up and the distillate for the first three minutes collected in a liquid nitrogen cold trap. The vacuum was then released, dry nitrogen was introduced into the system, and the material in the cold trap placed in an NMR tube. The smell of hydrogen cyanide was quite obvious. The NMR spectrum showed peaks at τ 2.7 (benzene) and very small peaks corresponding to those of tropylium azide.

Isolation of Free Amine By Column Chromatography

A sample of tropylium azide (10 ml) which had been irradiated six times (12 hrs.) was placed on a column of 200 g of Florisil. The tropylium azide was eluted with 2 liters of hexane. A white solid could sometimes be eluted with 500 ml of methylene chloride. The yield varied anywhere from zero to 50 milligrams of a white solid, mp 24-25°. Samples prepared in this way were used to determine the pK_a and an unsuccessful attempt was made to determine the Raman spectrum. The infrared spectrum (CCl_4) showed 3.46 μ (w), 3.53 μ (vw), 3.59 μ (vw), 6.12 μ (w), 6.30 μ (m), 7.20 μ (m), 7.73 μ (w), 7.92 μ (m), 8.25 μ (m), 8.52 μ (m), 9.00 μ (s), 9.18 μ (m), 9.65 μ (m), 9.89 μ (m), 13.82 μ (m), 14.20 μ (s), and 14.39 μ (vs).

Determination of pK_a of Free Amines

The pK_a of the free amine obtained by column chromatography was determined by titration of about 20 milligrams of the amine in 100 ml of distilled water, with 0.1 N hydrochloric acid. These titrations were carried out on a Sargent Model D Recording Titrimeter. Six of the determinations were carried out. The value of the pK_a is 5.14 ± 0.06 . All water used in this experiment was boiled to remove carbon dioxide and stored in sealed bottles until used.

CAUTION:

The use of methylene chloride has on occasion created problems. Methylene chloride has an identical chemical shift with that exhibited by the white solid reported in the original communication. When samples containing methylene chloride are not taken to dryness, misleading results can and have resulted. In the initial studies reported this troublesome impurity was clearly lacking because the work up nowhere employed this solvent.

APPENDIX IV

SYNTHESES OF AND A REARRANGEMENT IN TROPONE-IMINE SYSTEMS

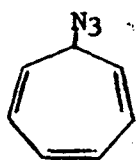
D. S. Wulfman, L. N. McCullagh, and J. J. Ward,
Chem. Commun., 220, (1970)

SYNTHESES OF AND A REARRANGEMENT IN TROPONE-IMINE SYSTEMS

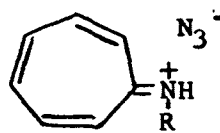
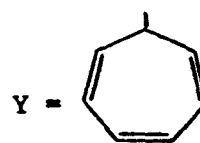
Summary

Tropyl azide (I) can be decomposed to form tropone-imonium azide (III) and N-tropyltropone-imonium azide (II); attempts to convert either salt or the corresponding fluoborates into tropone 2,4 dinitro-phenylhydrazone leads to the corresponding benzaldehyde derivative.

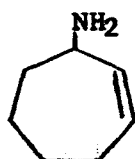
Attempts to elucidate the structure of an amine C_7H_7N , derivable from tropyl azide (I), have been complicated by the complexity of the reaction mixtures, low yields, and difficulty in obtaining reproducible results.¹ The compound $C_{14}H_{14}N_4$ obtained here and that reported in ref. 1 differ in several significant areas; 1H n.m.r. chemical shift and i.r. spectrum. Usually, vapour-phase photolysis of (I) using low-intensity u.v. sun-lamps furnishes small amounts of a white solid $C_7H_7N \cdot C_7H_7N_3$ (II) which exhibits λ_{max} (mull) 3.37, 3.42, 3.49, 4.74, 6.90, 7.03, 7.32, 7.98, 8.91, 9.34, 9.57, 11.2, 11.27, and 11.48 μm ; λ_{max} (EtOH) 236 (ϵ 10,000), 287 (2000) 3.7 (5000), and 325 (5500) nm, and shows a narrow multiplet in the 1H n.m.r. spectrum at τ 2.35 (6H)



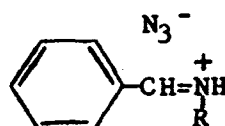
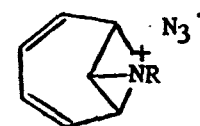
(I)

(II) R = Y
(III) R = H

Y =



(IV)

(V) R = Y
(VI) R = H(VII) R = Y
(VIII) R = H

as well as highly structured peaks at 3.34 (2H), 3.89 (2H), 4.63 (2H), and 5.95 (1H). These latter peaks resemble in considerable detail typical tropilidene n.m.r. spectra. Upon treatment of (II) with traces of acid (acetonitrile solution) a new peak occurs at τ 0.7 (7H). (The same location as tropylium ion.) Colorimetric analyses indicated the presence of one azide ion per molecule ($C_{14}H_{14}N_4$). Treatment of (II) with ethanol, followed by reaction with fluoboric acid, furnished tropone-imonium fluoborate identical in u.v. and i.r. spectra with a sample prepared by the method of Dauben.² The above appears to be consistent with the assignment of N-7-cycloheptatrienyltropone-immonium azide (II).

If a solution of (I) containing traces of (II) is allowed to stand several days at -20° , a copious light tan to brown precipitate (III) forms to the extent of 2-5%. This material had previously been treated by the method of Merling³ by one of us⁴ and also by Looker.⁵ Careful washing of (III) with cold pentane or methylene chloride ultimately freed it from traces of (I). This material showed a single structured singlet in the 1H n.m.r. spectrum (CD_3CN) at τ 2.35. The i.r. had λ_{max} (mull) 4.9, 6.1, 6.65, 6.7, 8.6 and 12.8 μm , and the u.v. showed λ_{max} (EtOH) 236, 3.6, and 325 nm. Acidification failed to alter the n.m.r. spectrum appreciably. Reduction using $NaBH_4$ - PtO_2 -EtOH furnished (IV), which was identified mass spectrometrically by comparison with an authenticated sample. The light tan solid can be readily converted into the fluoborate salt and other derivatives previously described by Bauld⁶ and subsequently by Dauben² and having similar melting points and spectral properties. Conversion of (III) into tropone was readily

realized and its i.r. and mass spectra were essentially identical with those from an authenticated sample and leads to the assignment of tropone-imonium azide for (III).

An attempt to determine if (V) or (VI) might be present (in principle to be expected from (VII) or (VIII)) was made using ethanolic phosphoric acid-2,4-dinitrophenylhydrazine reagent.⁷ A fair yield of benzaldehyde 2,4-dinitrophenylhydrazone (X) was obtained. Repetition using tropone-imonium fluoborate and 7-N-tropyltropone-imonium fluoborate furnished similar results. These are in strong contrast with the observations of Nozoe et al.⁸ with tropone and tropone oxime. A review of their reported melting points for the 2,4-dinitrophenylhydrazones and oximes from several tropones, and comparison with reported values for the expected rearrangement products, failed to uncover any ambiguous assignments. This type of rearrangement is not uncommon with tropylium salts in the presence of oxidants⁹ or when an incipient carbonium ion is present on a carbon α to C-7 in the tropilidene series.¹⁰ It does appear to be unique in the tropone, tropone-imine series.

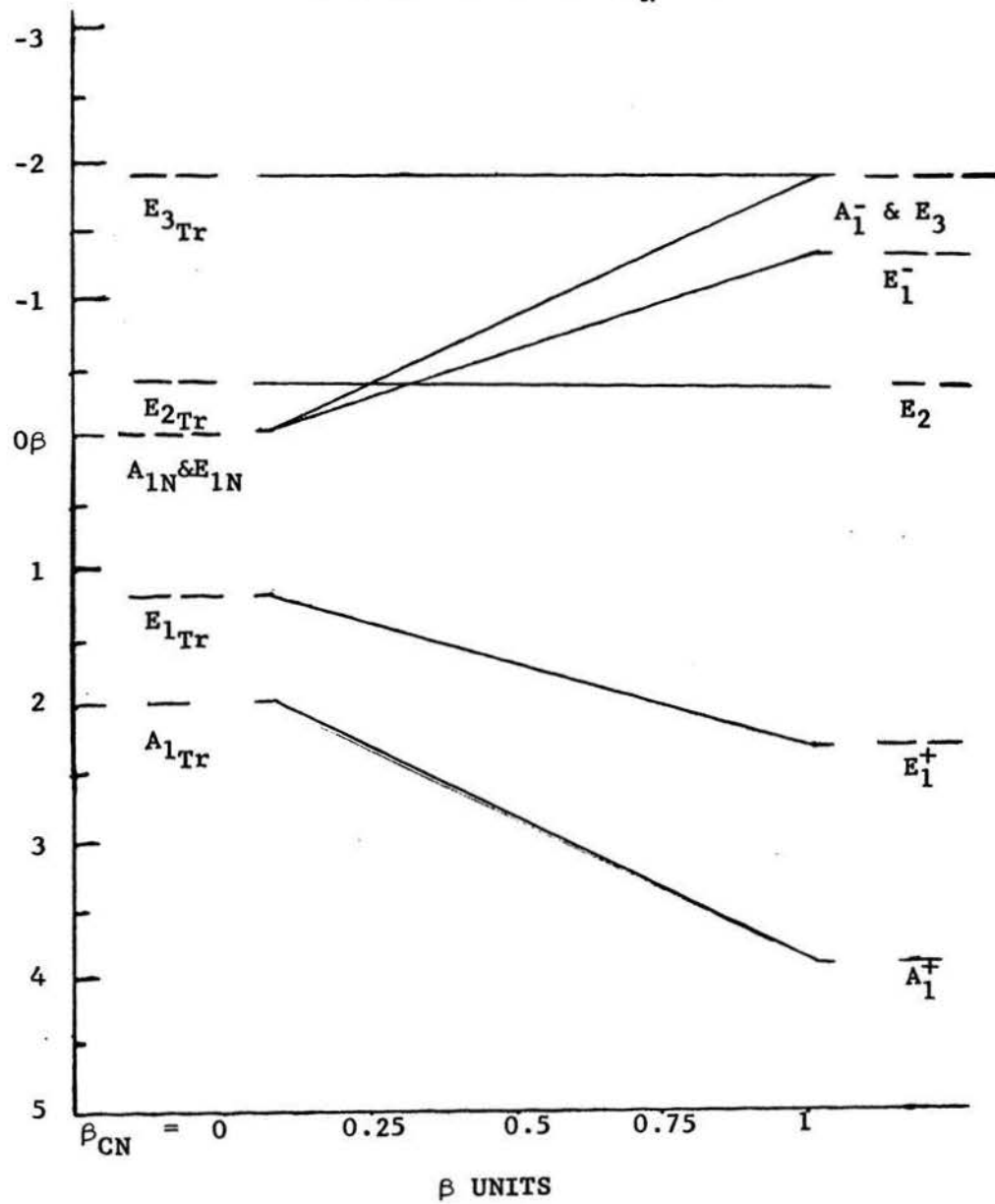
We have yet to succeed in isolating the other products(s) formed when (I) is converted into (III).

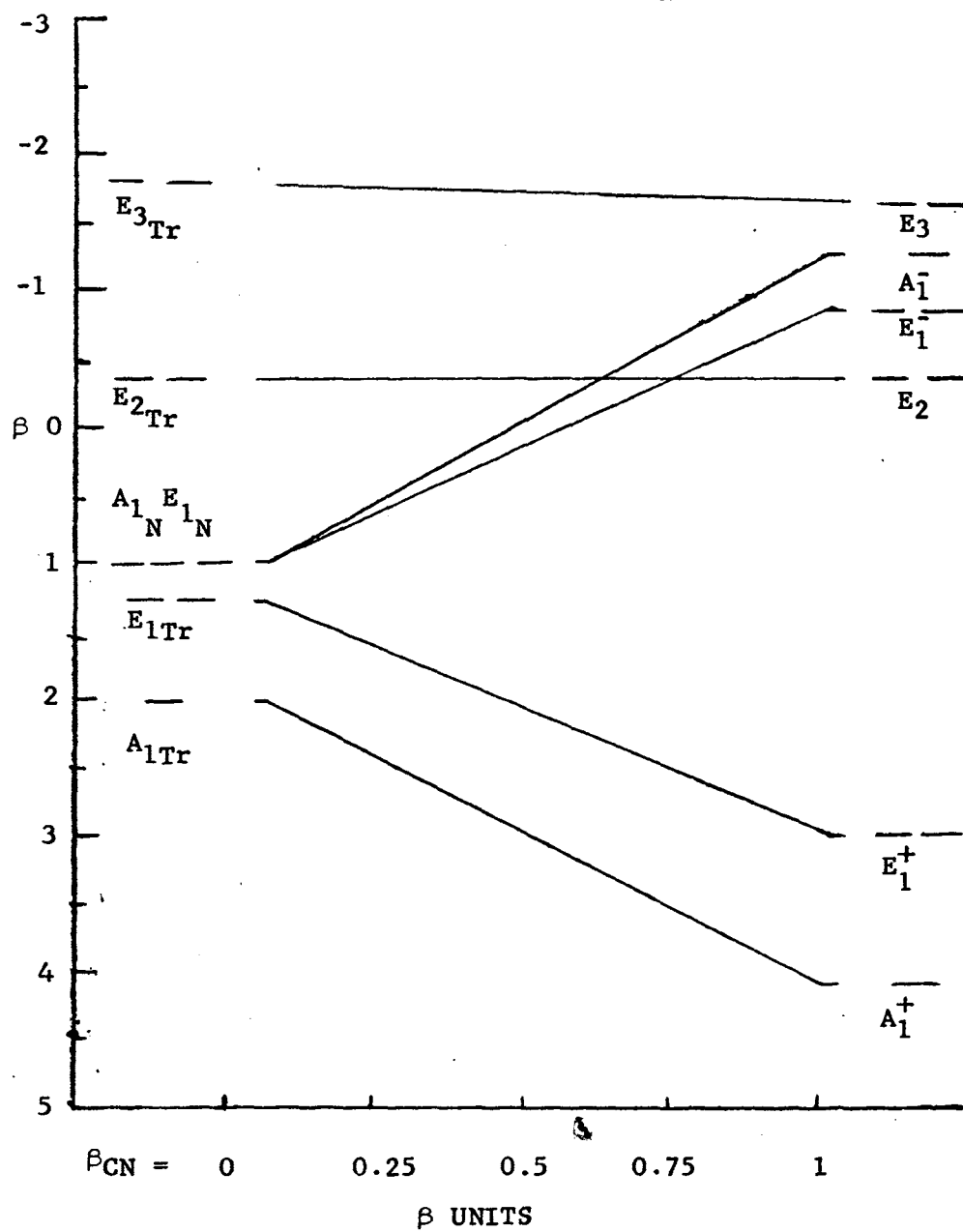
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APPENDIX V
CORRELATION DIAGRAMS FOR COMPOUND (19)

CORRELATION DIAGRAM $\alpha_N = 0$ 

CORRELATION DIAGRAM $\alpha_N = \beta$ 

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VIII. VITA

James Joseph Ward was born on October 10, 1943 in Pittsburg, Kansas. He received his elementary education in Pittsburg, Kansas and Webster Groves, Missouri and graduated from Chaffee High School at Chaffee, Missouri in 1961. He served active duty in the United States Army Reserve from June, 1961 to December, 1961. He received an Honorable Discharge as a Sergeant in the Standby Reserves on April 30, 1969. He entered Southeast Missouri State, Cape Girardeau, Missouri in January 1962 and completed one year. In February, 1963 he transferred to the University of Missouri - Rolla, where he received his Bachelor of Science degree with a major in Chemistry in January, 1966.

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